

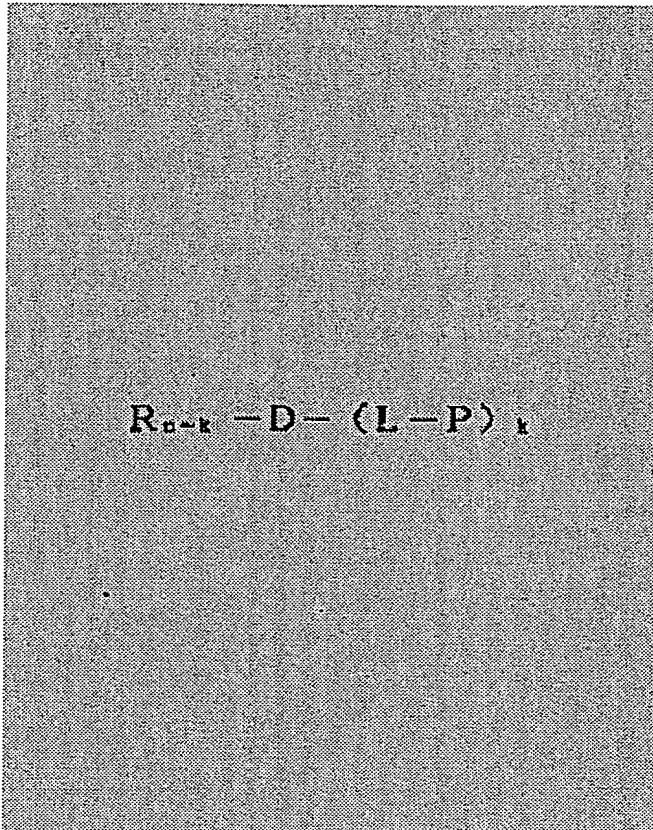
# PRODUCTION OF THIN FILM, OPTICALLY ANISOTROPIC SHEET AND LIQUID CRYSTAL DISPLAY DEVICE

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Applicant: FUJI PHOTO FILM CO LTD  
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## Abstract of JP8027284

PURPOSE: To obtain a thin film capable of providing an optically anisotropic sheet excellent in thermal durability and in monodomain property, and a phase difference film enabling the remarkable improvement in the angle of visibility used for liquid crystal elements by adding light or heat energy to a thin film containing a specific disk-like compound formed on a support.

CONSTITUTION: A light or heat energy is added to (C) a thin film containing (B) at least one kind of disk-like compound having a substituent capable of polymerizing by the addition of light or heat energy and formed on (A) a support to obtain the objective thin film. A thin film having an optically anisotropic molecular configuration or a thin film forming a discotic nematic liquid crystal phase is preferably used as the component C, and a compound of the formula [D is an n-valent functional group at the center of the molecule and radially having substituents of R and substituents of (P-L) in a total number of (n); kXP groups are isocyanate groups, etc.; (n-k)R groups are functional group not contributing to the polymerization composition; L is a bonding group connecting L to P and D, etc.], is preferably used as the component B.



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(33)優先権主張国	日本(JP)		
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最終頁に続く

(54)【発明の名称】 薄膜の製造方法

1 (57)【特許請求の範囲】

【請求項1】 表面上に配向膜を有する支持体の該配向膜上に、光または熱エネルギーを加えることにより重合し得る置換基を有する円盤状化合物を少なくとも1種含む塗布液を塗布、乾燥した後、該塗布された薄膜を加熱して光学的異方性の分子配向を有する薄膜とし、次いで光または熱エネルギーを加えることにより重合させて光学的異方性の薄膜を形成することからなる薄膜の製造方法。

【請求項2】 該光学的異方性の分子配向がディスコティックネマティック液晶層である請求項1に記載の薄膜の製造方法。

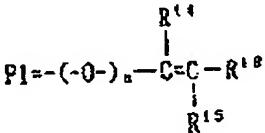
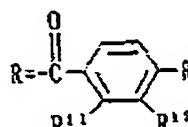
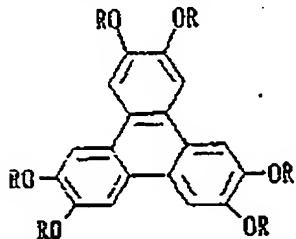
【請求項3】 該円盤状化合物が、下記一般式(1)で表わされ、反応性官能基Pをその放射状側鎖の末端に有する化合物である請求項1に記載の薄膜の製造方法。

2 一般式(1)

【化1】  $R_{n-k}-D-(L-P)_k$   
式中、Dは分子の中心にあり、合計n個の置換基R及び置換基-(L-P)を放射状に配するn官能の基を表わす。k個のPは各々独立に、イソシアート基、チオシアート基、アミノ基、アルキルアミノ基、アリールアミノ基、メルカプト基、ホルミル基、アシル基、水酸基、カルボキシル基、スルホ基、ホスホリル基、ハロカルボニル基、ハロスルホニル基、ハロホスホリル基、アクリロイル基、メタクリロイル基、クロトニル基、ビニルオキシ基、エポキシ基、アセチレン基、プロパギル基又はアレニル基を表わし、(n-k)個のRは各々独立に重合組成物の形成に寄与しない官能基を表わし、Lは各々独立に、PとDを連結する基もしくは化学結合を表わし、nは3~8の整数を表わし、そしてkは1~nの

整数を表わす。

【請求項4】 該円盤状化合物が、下記の一般式(2)、一般式(3)または一般式(4)で表わされる\*



式中、トリフェニレン環に結合する6つのベンゾイルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一個は置換基P1を有する。R<sup>11</sup>、R<sup>13</sup>は各々独立に水素原子またはメチル基を表わし、6個のR<sup>13</sup>は各々独立にアルコキシ基を表わし、その内の少なくとも一個は上記置換基P1を含むアルコキシ基\*

\*請求項1に記載の薄膜の製造方法。

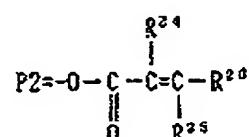
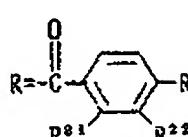
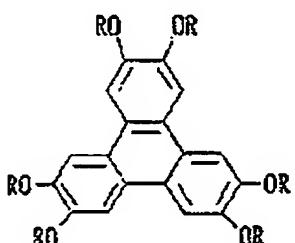
一般式(2)

【化2】

\*を表わし、置換基P1のR<sup>11</sup>、R<sup>13</sup>、R<sup>15</sup>は各々独立に水素原子またはアルキル基を表わし、そしてnは0または1を表わす。

一般式(3)

【化3】

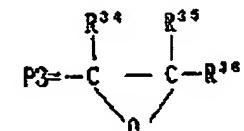
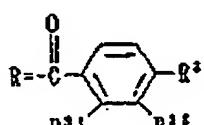
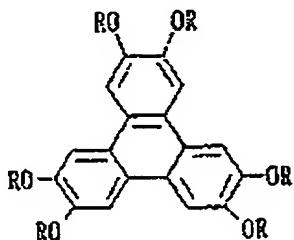


式中、トリフェニレン環に結合する6つのベンゾイルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一個は置換基P2を有する。R<sup>21</sup>、R<sup>23</sup>は各々独立に水素原子またはメチル基を表わし、6個のR<sup>23</sup>は各々独立にアルコキシ基を表わし、その内★

★の少なくとも一個は上記置換基P2を含むアルコキシ基を表わし、そして置換基P2のR<sup>24</sup>、R<sup>25</sup>、R<sup>26</sup>は各々独立に水素原子またはアルキル基を表わす。

一般式(4)

【化4】



式中、トリフェニレン環に結合する6つのベンゾイルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一個は置換基P3を有する。R<sup>31</sup>、R<sup>33</sup>は各々独立に水素原子またはメチル基を表わし、6個のR<sup>33</sup>は各々独立にアルコキシ基を表わし、その内の少なくとも一個は上記置換基P3を含むアルコキシ基を表わし、そして置換基P3のR<sup>34</sup>、R<sup>35</sup>、R<sup>36</sup>は各々独立に水素原子またはアルキル基を表わす。

【発明の詳細な説明】

#### [0001]

【産業上の利用分野】 本発明は、液晶表示装置、特にTN(ねじれネマティック)型液晶表示装置に有用な薄膜の製造方法に関する。

#### [0002]

【従来の技術】 従来、有機化合物分子を規則的に配向させる方法として、まずはX線結晶構造解析に用いられる单結晶の作成が挙げられる。また、一般的には界面活性剤のように親水部と疎水部を分子の両端に有する化合物

を水面に単分子層として展開したラングミュー・プロジェクト膜をすくいとて適当な支持体上に担持する方法。また構造的には似通っているが生体膜の模倣としての二分子膜の利用、さらに液晶表示素子の原理として利用されているもので適当な棒状分子を上下二枚の配向膜間隙に挟んで一方向・一定角度に自発的にあるいは磁界・電界を印加させて強制的に配向させる方法、また、蒸着した金薄膜の表面にアルカンチオールを並べる方法、写真用の分光増感に用いられる色素の会合する性質を利用して並べる方法など、様々な方法が挙げられる。

【0003】また、逆に配向秩序をもたせないいわゆるガラスあるいはアモルフォス状態を造成する方法も検討されている。それは、従来の化学が主に検討の対象としてきた単分子の性質とは異なる物理的・化学的・電気的・光学的に興味深い性質が分子の集合構造によって発現することに多くの関心が寄せられているからである。

【0004】しかし、先に述べた方法の対象となってきた有機化合物分子の構造はほとんどが棒状分子であった。本発明が対象とする円盤状分子とは、三次元的にこの棒状分子の逆の構造形態であることができる。円盤状分子は、ある原子あるいは分子をその中心核として数本の側鎖が放射状に伸びた構造、あるいはクラウンエーテルのような大環状構造、また脂肪族炭素骨格からなるコレステロールや芳香族炭素骨格からなるビレン、ナフタセンやコロネンなどの平板状構造などに分類できるが、平面構造ゆえπ-π相互作用、アルキル鎖の疎水性相互作用、核酸等での水素結合など、種々の分子間力が二次元的に作用するため、集合状態による性質は一層多岐にわたって興味深い性質を示す。

【0005】その代表的性質の一つとして、円盤状分子の上記分子間力に由来する液晶的性質が挙げられる。これらは総称してディスコティック液晶化合物と呼ばれるが、例えばベンゼン誘導体、トリフェニレン誘導体、トルキン誘導体、フタロシアニン誘導体、シクロヘキサン誘導体、アザクラウン系およびフェニルアセチレン系などのマクロサイクルが挙げられ、一般的にこれらを分子の中心の母核とし、直鎖のアルキル基やアルコキシ基、置換ベンゾイルオキシ基等比較的合成が容易な基がその側鎖として放射状に置換された構造のものが液晶状態を形成するものとして報告されているが、その熱的効率や液晶相の熱的安定性に関する知見は極めて少ない。

【0006】しかし、その興味深い集合状態の性質も、デバイス化してその機能を用いる場合、その耐久性の点で集合状態の安定性が大きな課題となる。以下に述べる光学異方性シートは、本発明の技術を応用した典型的例であり、上記の円盤状分子の構造的特徴を、すなわち単分子・集合状態の両方に起因する空間的因子状態に由来する特徴的光学機能を光学変調素子として活かした例であり、また、集合状態での固定化の重要性を示す例である。

【0007】日本語ワードプロセッサやデスクトップパソコン等のOA機器の表示装置の主流であるCRTは、薄型軽量、低消費電力という大きな利点をもった液晶表示素子に変換されてきている。現在普及している液晶表示素子（以下LCDと称す）の多くは、ねじれネマティック液晶を用いている。このような液晶を用いた表示方法としては、複屈折モードと旋光モードとの2つの方式に大別できる。

【0008】複屈折モードを用いたLCDは、液晶分子配列のねじれ角が90°以上ねじれたもので、急峻な電気光学特性をもつ為、能動素子（薄膜トランジスタやダイオード）が無くても単純なマトリックス状の電極構造で時分割駆動により大容量の表示が得られる。しかし、応答速度が遅く（数百ミリ秒）、階調表示が困難という欠点を持ち、能動素子を用いた液晶表示素子（TFT-LCDやMIM-LCDなど）の表示性能を越えるまでには至らない。

【0009】TFT-LCDやMIM-LCDには、液晶分子の配列状態が90°ねじれた旋光モードの表示方式（TN型液晶表示素子）が用いられている。この表示方式は、応答速度が速く（数十ミリ秒）、容易に白黒表示が得られ、高い表示コントラストを示すことから他の方式のLCDと比較して最も有力な方式である。しかし、ねじれネマティック液晶を用いていたり、表示方式の原理上、見る方向によって表示色や表示コントラストが変化するといった視角特性上の問題点があり、CRTの表示性能を越えるまでには至らない。

【0010】特開平4-229828号、特開平4-258923号公報などに見られるように、一対の偏光板とTN型液晶セルの間に、位相差フィルムを配置することによって視野角を拡大しようとする方法が提案されている。上記特許公報で提案された位相差フィルムは、液晶セルに対して、垂直な方向に位相差がほぼゼロのものであり、真正面からはなんら光学的な作用を及ぼさず、傾けたときに位相差が発現し、液晶セルで発現する位相差を補償しようとするものである。しかし、これらの方法によつてもLCDの視野角はまだ不十分であり、更なる改良が望まれている。特に、車載用や、CRTの代替として考えた場合には、現状の視野角では全く対応できないのが現状である。

【0011】また、特開平4-366808号、特開平4-366809号公報では、光学軸が傾いたカイラルネマティック液晶を含む液晶セルを位相差フィルムとして用いて視野角を改良しているが、2層液晶方式となりコストが高く、非常に重いものになっている。さらに特開平5-80323号公報に、液晶セルに対して、光軸が傾斜している位相差フィルムを用いる方法が提案されているが、一軸性のポリカーボネートを斜めにスライスして用いているため、大面積の位相差フィルムを、低コストで得難いという問題点があった。

【0012】さらに、特願平5-5823号明細書に光異性化物質を用いて光軸が傾斜している位相差フィルムを用いる方法が記載されている。この方法によれば、広い視野角特性を有し、軽量で、かつ低コストの液晶表示素子が実現できる。しかし、この方法の欠点として該位相差フィルムの熱・光に対する安定性が十分でないという問題点があった。

【0013】特開平5-215921号公報においては、一对の配向処理された基板に硬化時に液晶性を示す棒状化合物を挟持した形態の複屈折板によりLCDの光学補償をする案が提示されているが、この案では従来から提案されているいわゆるダブルセル型の偏光板と何等変わることなく、大変なコストアップになり、事実上大量生産には向かない。さらに棒状化合物を使用する限りは、後に述べる光学的理由によりその複屈折板ではTN型LCDの全方位の視野角改善は不可能である。

【0014】また、特開平3-9326号、及び特開平3-291601号公報においては、配向膜が設置されたフィルム状基板に高分子液晶を塗布することによりLCD用の光学補償板とする案が記載されているが、この方法では分子を斜めに配向させることは不可能であるため、やはりTN型LCDの全方位の視野角改善は不可能である。

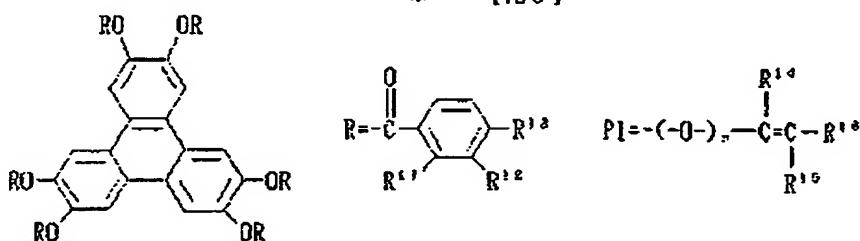
【0015】そこで、本発明者は、特願平5-236539号明細書によりディスコティック液晶化合物を配向膜により配向させると、その薄膜の光軸が斜めに傾斜し、光学偏光シートとして有用であることを示した。しかし、最近では、液晶表示素子は、自動車のダッシュボードの計器表示板やカーナビゲーション用液晶テレビとして用いられるようになってきており、益々高い熱的耐久性が要求されている。

#### 【0016】

【発明が解決しようとする課題】本発明の目的は、液晶表示装置、特にTN(ねじれネマティック)型液晶表示装置に有用な熱的耐久性に優れた薄膜の製造方法を提供することにある。

#### 【0017】

\*



【0021】式中、トリフェニレン環に結合する6つのベンジルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一個は置換基P1を有する。

R<sup>1</sup>、R<sup>2</sup>は各々独立に水素原子またはメチル基を表わし、6個のR<sup>3</sup>は各々独立にアルコキシ基を表わ

\* 【課題を解決するための手段】本発明は、表面に配向膜を有する支持体の該配向膜上に、光または熱エネルギーを加えることにより重合し得る置換基を有する円盤状化合物を少なくとも1種含む塗布液を塗布、乾燥した後、該塗布された薄膜を加熱して光学的異方性の分子配向を有する薄膜とし、次いで光または熱エネルギーを加えることにより重合させて光学的異方性の薄膜を形成することからなる薄膜の製造方法にある。上記製造方法の好ましい感想は下記のとおりである。

1) 光学的異方性の分子配向がディスコティックネマティック液晶層である。

2) 円盤状化合物が、下記一般式(1)で表わされ、反応性官能基Pをその放射状側鎖の末端に有する化合物である。

一般式(1)

【0018】

【化5】

R<sub>n-k</sub>-D-(L-P),

【0019】式中、Dは分子の中心にあり、合計n個の置換基R及び置換基-(L-P)を放射状に配するn官能の基を表わす。k個のPは各々独立に、イソシアナート基、チオシアナート基、アミノ基、アルキルアミノ基、アリールアミノ基、メルカブト基、ホルミル基、アシル基、水酸基、カルボキシル基、スルホ基、ホスホリル基、ハロカルボニル基、ハロスルホニル基、ハロホスホリル基、アクリロイル基、メタクリロイル基、クロトニル基、ビニルオキシ基、エポキシ基、アセチレン基、プロパギル基又はアレニル基を表わし、(n-k)個のRは各々独立に重合組成物の形成に寄与しない官能基を表わし、Lは各自独立に、PとDを連結する基もしくは化学結合を表わし、nは3~8の整数を表わし、そしてkは1~nの整数を表わす。

3) 円盤状化合物が、下記の一般式(2)、一般式(3)または一般式(4)で表わされる。

一般式(2)

【0020】

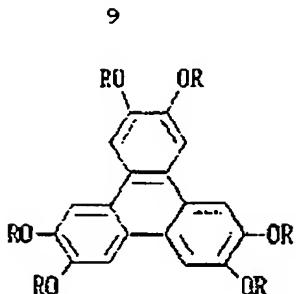
【化6】

し、その内の少なくとも一個は上記置換基P1を含むアルコキシ基を表わし、置換基P1のR<sup>11</sup>、R<sup>12</sup>、R<sup>13</sup>は各々独立に水素原子またはアルキル基を表わし、そしてnは0または1を表わす。

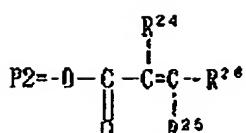
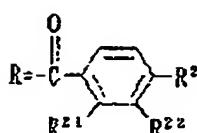
一般式(3)

50

【0022】



\* \* 【化7】



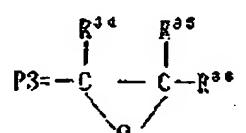
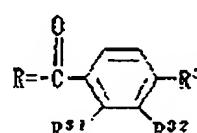
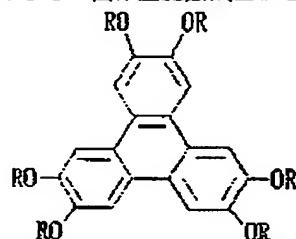
【0023】式中、トリフェニレン環に結合する6つのベンゾイルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一個は置換基P2を有する。R<sup>21</sup>、R<sup>23</sup>は各々独立に水素原子またはメチル基を表わし、6個のR<sup>23</sup>は各々独立にアルコキシ基を表わし、その内の少なくとも一個は上記置換基P2を含むア※

10※ルコキシ基を表わし、そして置換基P2のR<sup>24</sup>、R<sup>25</sup>、R<sup>26</sup>は各々独立に水素原子またはアルキル基を表わす。

一般式(4)

【0024】

【化8】



【0025】式中、トリフェニレン環に結合する6つのベンゾイルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一個は置換基P3を有する。R<sup>31</sup>、R<sup>33</sup>は各々独立に水素原子またはメチル基を表わし、6個のR<sup>33</sup>は各々独立にアルコキシ基を表わし、その内の少なくとも一個は上記置換基P3を含むアルコキシ基を表わし、そして置換基P3のR<sup>34</sup>、R<sup>35</sup>、R<sup>36</sup>は各々独立に水素原子またはアルキル基を表わす。

【0026】以下に、本発明を詳しく説明する。円盤状化合物は、構造的特徴からの総称であるが、物性的には、自己配向性を有するいわゆるディスコティック液晶性化合物と非液晶性化合物に分類することができる。但し、両方の物性を構造から分類することは困難である。円盤状化合物でかつディスコティック液晶化合物として代表的なものは例えば、C. Destraadeらの研究報告、Mol. Cryst. Liq. Cryst. 71巻、111頁(1981年)に記載されている。ベンゼン誘導体、トリフェニレン誘導体、トルキセン誘導体、フタロシアニン誘導体や、B. Kohnneらの研究報告、Angew. Chem. 96巻、70頁(1984年)に記載されたシクロヘキサン誘導体及びJ. M. Lehnらの研究報告、J. Chem. Soc. Chem. Commun., 1794頁(1985年)、J. Zhangらの研究報告、J. Am. Chem. Soc. 116巻、2655頁(1994年)に記載されているアザクラウン系やフェニルアセチレン系マクロサイ

クルが挙げられ、一般的にこれらを分子の中心の母核とし、直鎖のアルキル基やアルコキシ基、置換ベンゾイルオキシ基等がその側鎖として放射状に置換された構造である。

【0027】この他、日本化学会編 化学総説 第22巻、液晶の化学 135頁(1994年)に記載されている有機金属錯体のディスコティック液晶が挙げられる。これらは、分子の中心に金属原子を配し、その配位子が同一平面上に金属を囲むように位置することによってディスコティック液晶性挙動を示すと考えられる。

【0028】一方、円盤状化合物であるが、非液晶性化合物の例としては、日本化学会第69春季年会講演予稿集II 3A111, 3A112, 3A113, 3A114に記載されるガラス共役系分子、1G241, 1G242, 1G243に記載のシクロファン分子などが挙げられる。

【0029】本発明者は、これらの円盤状化合物に関して、その液晶化合物の配向状態と光学特性の対応を詳細に研究し、液晶セルの全ての視野角からの表示品位を最適に改善するためには、光学的に一軸配向したディスコティック液晶分子の傾斜角分布を液晶セルの特性に適応するように制御することが必要であることがわかった。

【0030】ディスコティック液晶相は、一般に円板状分子の中心コアが分子間力で柱状に積み重なった柱状相(columnar phase)と、円板状分子が乱雑に凝集したディスコティックネマティック相と、カイラルディスコティックネマティック相に大別できること

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が知られている。しかし、W. H. de Jeu著のPhysical properties of liquid crystalline materials (1980 by Gordon and Breach, Science Publishers)に記載されているように、柱状相はしばしば見出されるが、ディスコティックネマティック相は稀にしか見出されていない。

【0031】また、本発明のトリフェニレン系ディスコティック液晶が負の複屈折を有することは、B. Moreyらの研究報告 [Mol. Cryst. Liq. Cryst., 84巻, 193頁(1982年)]で明かにされているが、実際にこの性質を光学偏光シートとして応用するためには、片面支持体上でその薄膜を構成する分子全体が室温状態で統計的に一方向に並んだ状態を実現することが必要である。一般的に、ディスコティック液晶は従来の柱状分子からなる液晶と同様に、微視的には特定の方向性をもった配向領域(ドメイン)で構成され、巨視的には光学的異方性を示さず光散乱性のいわゆるマルチドメイン相を形成するという性質があるため、多くの場合にその薄膜は光学偏光シートに利用できるほどの好ましい光学的特性を示さない。

【0032】この点に関して、恒々のディスコティック液晶のうち、ディスコティックネマティック液晶相または一軸性の柱状相を形成する性質を有する液晶としては、トルキセン誘導体、トリフェニレン誘導体及びフェニルアセチレン系マクロサイクルが挙げられるが、なかでもトリフェニレン誘導体は、合成も容易で、光学素子として利用する上で有利なモノドメイン性のディスコティックネマティック相を形成し易い。

【0033】トリフェニレン誘導体とは、一般的には、一般式(2)、一般式(3)や一般式(4)に示す様にベンゼン環の周囲にさらに3つのベンゼン環が放射状に縮合した構造を指し、報告されている液晶化合物の中では、アルコキシ基、アルカノイルオキシ基、ベンジルオキシ基が、2、3、6、7、10、11一位に置換した化合物がほとんどである。そしてこのトリフェニレン誘導体の特徴は、他のディスコティック液晶に比べてモノドメイン性のディスコティックネマティック相を形成しやすいことである。光学的に異方性であるためには、統計的に光軸がある方向に傾いている必要があります。そのためには液晶の一般的な性質とも言えるマルチドメインの形成を抑制してモノドメイン性の液晶相の形成が必要である。従って、モノドメイン性のディスコティックネマティック相を形成しやすいトリフェニレン誘導体は、上記の理由で光学異方素子としての可能性が相対的に大きな化合物群であると考えられる。

【0034】特願平5-295501号明細書に開示したように、このディスコティック液晶はポリイミドなど恒々の配向膜上に塗布し、液晶化温度以上に加熱すること

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により容易に配向し、また、その状態で急冷することにより、その配向状態を保持したまま、ガラス状態で安定に存在する。しかも、その状態での屈折率異方性の測定から、ディスコティック液晶分子が配向膜のラビング方向に一様に傾斜したように配向していることが推察された。柱状の液晶分子では、液晶セルのような2枚の配向膜間の各界面でチルト角が誘起された状態で一方向に配向させができるが、ディスコティック液晶では唯一枚の配向膜上で同様のチルト角が誘起される。さらに特願平6-70591号に開示したように、そのディスコティック液晶を主成分とし、別の有機化合物を混合することでそのチルト角を制御できることは大きな特徴である。従って、そのようにして形成したディスコティック液晶薄膜は、光軸が傾斜し負の複屈折性を明瞭に示す光学的異方性シートであり、液晶表示素子用位相差膜として有用であることも明らかにした。

【0035】本発明の光または熱エネルギーを加えることにより重合し得る置換基としては、例えばS. R. SandlerおよびW. Karo (S. R. Sandler, W. Karo) 著、オーガニック ファンクショナル グループ プレバレーションズ (Organic Functional Group Preparations) 第1巻および第2巻 (アカデミックプレス社、ニューヨーク、ロンドン1968年刊) に記載の置換基を挙げることができる。それらのうち好ましくは、多重結合、オキシラン、アシリジンであり、さらに好ましくはR. A. M. Hikmetらの研究報告 [Macromolecules, 25巻, 4194頁(1992年) ] 及び [Polymer, 34巻, 8号, 1736頁(1993年) ] 、D. J. Broerらの研究報告 [Macromolecules, 26巻, 1244頁(1993年) ] に記載されているように、二重結合すなわちアクリル基、ビニルエーテル基およびエポキシ基である。

【0036】本発明の前記(4)の一般式(1)に記載した、重合反応に寄与する反応性官能基Pと中心核Dを連結するLは、一般に化学結合やオキシ基より、重合により生じる体積歪みを緩和しやすい官能基、例えばアルキレン基、アルキレンオキシ基、アルキレンチオ基、アルキレンアミノ基、オリゴエチレンオキシ基などが好ましい。実際に、シンナモイル基を光重合性基としてトリフェニレン核に連結した液晶性化合物は、紫外光照射による重合過程で、照射前の配向状態が著しく損なわれることが判っている。

【0037】一方、重合組成物の形成に寄与しない置換基Rは、重合反応に結果的に寄与しなかった基を意味するものであり、従って、置換基(L-P)の構造も含んでよいし、その類似の構造すなわち一般的に重合反応に寄与できないハロゲン原子、ニトロ基、シアノ基、アルコキシ基などが置換あるいは無置換のアルキル基、アリ

13

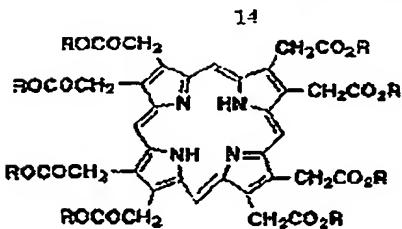
ール基、アラルキル基、アルキルチオ基、アリールチオ基、アリールアミノ基、アルキルアミノ基、アルゴキシ基、アリールオキシ基、ベンゾイルオキシ基が挙げられる。

【0038】しかし、我々の検討によれば、温か条件で重合反応が進行するという点で、重合反応に寄与できる基が多いほど高い耐久性が得られており、好ましい。また、全ての側鎖にアクリロイル基をもつトリフェニレン環化合物で、十分な重合反応が進行したのちの重合組成物中にかなりのアクリロイル基が残存していることが観察された例もあり、必ずしも全ての反応性基が重合に寄与していないことが示唆される。

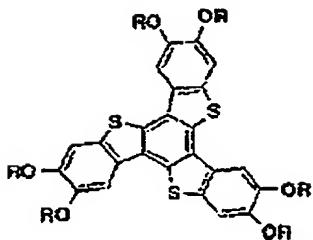
【0039】以下に、一般式(1)で表される本発明の化合物の具体例を示すが、これによって本発明が限定されることはない。

【0040】

【化9】



	DLC-NO.	R
10	DLC-1	$-C_2H_4OCOCH=CH_2$
	DLC-2	$-C_4H_6OCOCH=CH_2$
	DLC-3	$-C_6H_{12}OCOCH=CH_2$
	DLC-4	$-C_9H_{16}OCOCH=CH_2$
20	DLC-5	$-C_2H_4OC\equiv CH$
	DLC-6	$-C_4H_6OCH_2C\equiv CH$
	DLC-7	$-C_6H_{12}OCH_2CH_2$
	DLC-8	$-C_9H_{16}OCH_2CH_2$
30	DLC-9	$-C_2H_4OCH_2CH_2NH_2$
	DLC-10	$-C_4H_6SO_3H$
	DLC-11	$-C_6H_{12}OCH_2CH(CH_3)OC$
	DLC-12	$-C_9H_{16}OCH_2CH(CH_3)OC$
40	【0041】	
	【化10】	



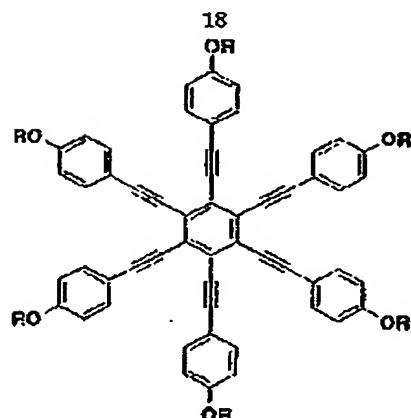
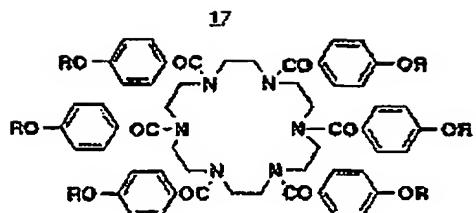
## DLC-NO.

R

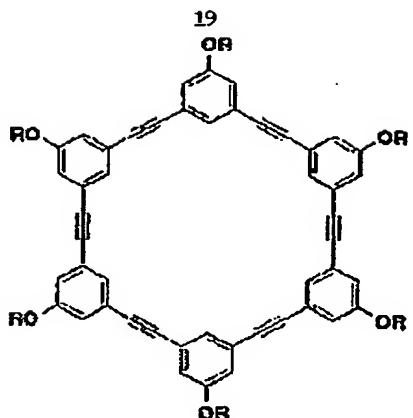
DLC-13	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}_2\text{H}_4\text{OCOC}=\text{CH}_2 \end{array}$
DLC-14	$-\text{C}_4\text{H}_8\text{OCOCH}=\text{CH}_2$
DLC-15	$-\text{C}_6\text{H}_{12}\text{OCOCH}=\text{CH}_2$
DLC-16	$-\text{C}_9\text{H}_{18}\text{OCOCH}=\text{CHCH}_3$
DLC-17	$-\text{C}_2\text{H}_4\text{OCH}=\text{CH}_2$
DLC-18	$-\text{C}_4\text{H}_8\text{OCH}=\text{CH}_2$
DLC-19	$-\text{C}_6\text{H}_{12}\text{OCONHC}_2\text{H}_4\text{NCS}$
DLC-20	$-\text{C}_9\text{H}_{18}\text{OCH}=\text{CH}_2$
DLC-21	$-\text{C}_2\text{H}_4\text{SC}_2\text{H}_4\text{SH}$
DLC-22	$-\text{C}_4\text{H}_8\text{CHO}$
DLC-23	$-\text{C}_6\text{H}_{12}\text{OCH}_2\text{CH}-\text{CH}_2\text{O}$
DLC-24	$-\text{C}_9\text{H}_{18}\text{OCH}_2\text{CH}-\text{CH}_2\text{O}$

[0042]

[化11]



DLC-NO.	R	16	DLC-NO.	R
DLC-25	$-C_2H_4OCOCH=CH_2$		DLC-37	$-C_6H_5OCOCH=CH_2$
DLC-26	$-C_6H_5OCOCH=CH_2$		DLC-38	$-C_6H_{12}OCOCH=CH_2$
DLC-27	$-C_6H_{12}OCOCH=CH_2$		DLC-39	$-C_2H_4OCH=CH_2$
DLC-28	$-C_9H_{10}OH$		DLC-40	$-C_2H_4OCH=CH_2$
DLC-29	$-C_2H_4OCH=CH_2$	26	DLC-41	$-C_6H_{12}OCH=CH_2$
DLC-30	$-C_4H_8CO_2H$		DLC-42	$-C_9H_{10}OCH=CH_2$
DLC-31	$-C_6H_{12}OCH=CH_2$		DLC-43	$-C_2H_4OCH_2CH=CH_2$
DLC-32	$-C_9H_{10}OCH=CH_2$		DLC-44	$-C_4H_8OCH_2CH=CH_2$
DLC-33	$-C_2H_4OCH_2CH=CH_2$	30	DLC-45	$-C_6H_{12}OCH_2CH=CH_2$
DLC-34	$-C_4H_8OCH_2CH=CH_2$			
DLC-35	$-C_6H_{12}OCH_2C\equiv CH$			
DLC-36	$-C_9H_{10}OCH_2CH=CH_2$			
[0043]		40 [0044]		
[化12]				[化13]

[0045]  
[化14]

10

DLC-NO.

R

DLC-46  $-C_4H_9OCOCH=CH_2$ DLC-47  $-C_6H_{12}OCOCH=CH_2$ 

20

DLC-48  $-C_9H_{18}OCOCH=CH_2$ DLC-49  $-C_2H_4OCH=CH_2$ DLC-50  $-C_6H_{12}OCH=CH_2$ DLC-51  $-C_9H_{18}OCH=CH_2$ 

30

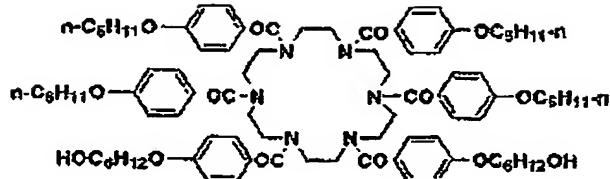
DLC-52  $-C_2H_4OCH_2CH\cdot CH_2$   
DLC-53  $-C_4H_8OCN_2CH\cdot CH_2$   
DLC-54  $-C_6H_{12}OCH_2CH\cdot CH_2$

(11)

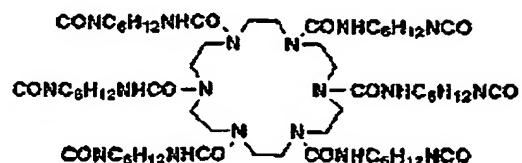
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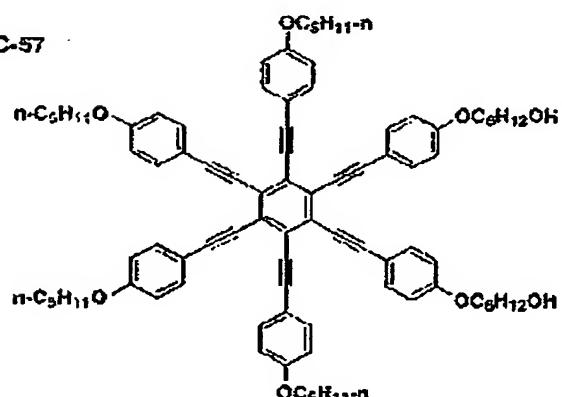
DLC-55



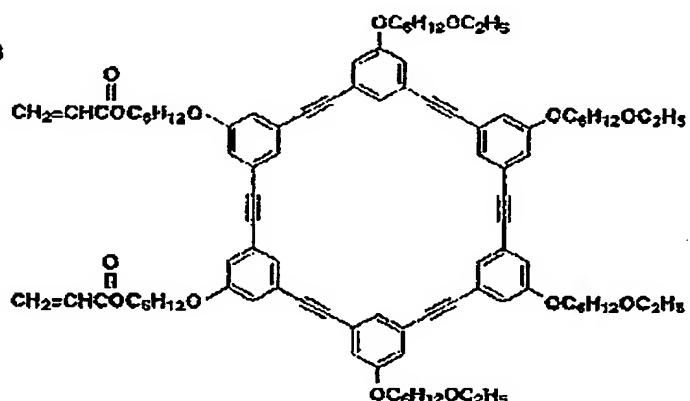
DLC-56



DLC-57

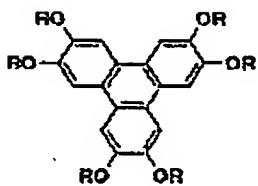


DLC-58



【0046】

【化15】



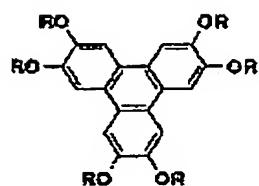
## DLC-NO.

R

DLC-59  $-C_2H_4OCOCH=CH_2$ DLC-60  $-C_4H_8OCOCH=CH_2$ DLC-61  $-C_6H_{12}OCOCH=CH_2$ DLC-62  $-C_9H_{18}OH$ DLC-63  $-C_2H_4OCH=CH_2$ DLC-64  $-C_4H_8CO_2H$ DLC-65  $-C_6H_{12}OCH=CH_2$ DLC-66  $-C_9H_{18}OCH=CH_2$ DLC-67  $-C_2H_4OCH_2CH-\overset{\text{O}}{\text{C}}\text{H}_2$ DLC-68  $-C_4H_8OCH_2CH-\overset{\text{O}}{\text{C}}\text{H}_2$ DLC-69  $-C_6H_{12}OCH_2C\equiv CH$ DLC-70  $-C_9H_{18}OCH_2CH-\overset{\text{O}}{\text{C}}\text{H}_2$ 

[0047]

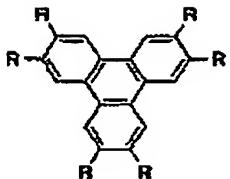
[化16]



DLC-NO.	R
DLC-71	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}_2\text{H}_4\text{OCOCC=CH}_2 \end{array}$
DLC-72	$-\text{C}_4\text{H}_6\text{OCOCH=CH}_2$
DLC-73	$-\text{C}_8\text{H}_{12}\text{OCOCH=CH}_2$
DLC-74	$-\text{C}_9\text{H}_{16}\text{OCOCH=CHCH}_3$
DLC-75	$-\text{C}_2\text{H}_4\text{OCH=CH}_2$
DLC-76	$-\text{C}_4\text{H}_6\text{OCH=CH}_2$
DLC-77	$-\text{C}_8\text{H}_{12}\text{OCCONHC}_2\text{H}_4\text{NCS}$
DLC-78	$-\text{C}_9\text{H}_{16}\text{OCH=CH}_2$
DLC-79	$-\text{C}_2\text{H}_4\text{SC}_2\text{H}_4\text{SH}$
DLC-80	$-\text{C}_4\text{H}_8\text{CHO}$
DLC-81	$-\text{C}_8\text{H}_{12}\text{OCH}_2\text{CH}-\text{CH}_2$   O
DLC-82	$-\text{C}_9\text{H}_{16}\text{OCH}_2\text{CH}-\text{CH}_2$   O

【0048】

【化17】



## DLC-NO.

R

DLC-83	$\text{CH}_3$   $-\text{OC}_2\text{H}_4\text{OCOCH}=\text{CH}_2$
DLC-84	$-\text{OC}_5\text{H}_{10}\text{OCOCH}=\text{CH}_2$
DLC-85	$-\text{NHC}_6\text{H}_{12}\text{OCOCH}=\text{CH}_2$
DLC-86	$-\text{OC}_6\text{H}_{12}\text{OCOCH}=\text{CHCH}_3$
DLC-87	$-\text{NHC}_2\text{H}_4\text{OCH}=\text{CH}_2$
DLC-88	$-\text{OC}_3\text{H}_6\text{OCH}=\text{CH}_2$
DLC-89	$-\text{OC}_6\text{H}_{12}\text{OCOCONHC}_2\text{H}_4\text{NCO}$
DLC-90	$\text{C}_2\text{H}_5$   $-\text{OC}_2\text{H}_4\text{CHC}_3\text{H}_6\text{OCH}=\text{CH}_2$
DLC-91	$-\text{SC}_2\text{H}_4\text{SC}_2\text{H}_4\text{SH}$
DLC-92	$-\text{SC}_2\text{H}_4\text{CHO}$
DLC-93	$-\text{SC}_6\text{H}_{12}\text{OCH}_2\text{CH}-\text{CH}_2$   O
DLC-94	$-\text{SC}_9\text{H}_{18}\text{OCH}_2\text{CH}-\text{CH}_2$   O

【0049】また、以下に、一般式(1)で表される本発明の化合物の番号(DLC-No.)と組合して用いられる化合物の構造例を示す。

【0050】

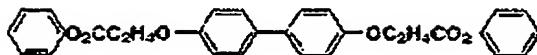
【化18】

29  
DLC-NO.

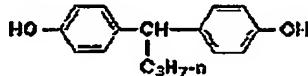
## 混合物の構造

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DLC-9



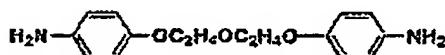
DLC-11



DLC-19



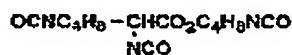
DLC-22



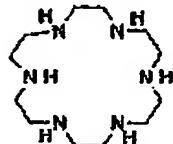
DLC-20



DLC-55



DLC-58



【0051】本発明の前記〔5〕の一般式(2)、一般式(3)及び一般式(4)で表される化合物は、そのような重合性の置換基をその側鎖に少なくとも一つ有し、その中心にトリフェニレン系炭素骨格構造を有するものである。その導歴が、光学的異方性材料として好ましい特性をもっており、さらに光あるいは熱による重合により得られる薄膜は重合前の配向が維持されるため、光学特性と耐熱性を両立できるものと考えられる。

【0052】以下に、一般式(2)について、詳細に説明する。R<sup>11</sup>、R<sup>12</sup>は、各々独立に水素原子またはメチル基を表す。nが0の時は、置換基P1は不飽和の二重結合基を表す。その置換基R<sup>13</sup>、R<sup>14</sup>は、各々独立に水素原子、アルキル基(例えばメチル、エチル、n-ブロピル、イソブロピル、n-ブチル、ベンチル、ヘキシル、ヘプチル、オクチル、ノニル、2-クロロエチル、3-メトキシエチル、メトキシエトキシエチルが挙げられ、メチル、エチルなどの低級アルキル基が好ましく、さらにメチルが好ましい。)を表し、R<sup>13</sup>がメチル基でR<sup>14</sup>が水素原子、またはR<sup>13</sup>、R<sup>14</sup>が共に水素原子の組み合わせが好ましい。

【0053】置換基R<sup>15</sup>は水素原子、置換または無置換のアルキル基(例えばメチル、エチル、n-ブロピル、

30 イソブロピル、n-ブチル、ベンチル、ヘキシル、ヘプチル、オクチル、ノニル、2-クロロエチル、3-メトキシエチル、メトキシエトキシエチルが挙げられ、メチル、エチルなどの低級アルキル基が好ましく、さらにメチルが好ましい。)を表し、水素原子、低級アルキル基が好ましく、さらに水素原子が好ましい。

【0054】式中、トリフェニレン環に結合する6つのベンゾイルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一つは置換基P1を有する。6つのR<sup>16</sup>は各々独立にアルコキシ基(例えばエトキシ、プロポキシ、ブロキシ、ペントキシ、ヘキシルオキシ、ヘブチルオキシ)、置換アルコキシ基(例えば、エチレンオキシエトキシ)を表す。

【0055】6つのR<sup>16</sup>のうち少なくとも一つは末端置換基P1が置換して成るアルコキシ基であるが、P1を連結する基は、アルキレンオキシ基(例えばエチレンオキシ、プロピレンオキシ、ブチレンオキシ、ベンチレンオキシ、ヘキシレンオキシ、ヘブチレンオキシ)、置換アルキレンオキシ基(例えばエチレンオキシエトキシ)を表す。置換基P1を有する側鎖は多いほど好ましい。

但し、末端置換基P1が直接芳香環に結合してもよい。

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【0056】 $\alpha$ が1の時は、 $R^{11}$ の末端置換基P1はいわゆるビニルエーテル基を表す、その置換基P1の置換基 $R^{11}$ 、 $R^{12}$ は、各々独立に水素原子、アルキル基（例えばメチル、エチル、n-ブロビル、イソブロビル、n-アブチル、ベンチル、ヘキシル、ヘブチル、オクチル、ノニルが挙げられ、メチル、エチルなどの低級アルキル基が好ましく、さらにメチルが好ましい。）を表し、 $R^{11}$ がメチル基で $R^{12}$ が水素原子、または $R^{11}$ 、 $R^{12}$ が共に水素原子の組み合わせが好ましい。

【0057】置換基 $R^{10}$ は水素原子、置換または無置換のアルキル基（例えばメチル、エチル、n-ブロビル、イソブロビル、n-アブチル、ベンチル、ヘキシル、ヘブチル、オクチル、ノニル、2-クロロエチル、3-メトキシエチル、メトキシエトキシエチルが挙げられ、メチル、エチルなどの低級アルキル基が好ましく、さらにメチルが好ましい。）を表し、水素原子、低級アルキル基が好ましく、さらに水素原子が好ましい。従って、置換基P1としては、一般には重合活性の高い官能基である無置換のビニルオキシ基が好ましく用いられる。

【0058】その末端置換基P1が置換して成るアルコキシ基は、アルキレンオキシ基（例えばエチレンオキシ、ブロビレンオキシ、ブチレンオキシ、ベンチレンオキシ、ヘキシレンオキシ、ヘブチレンオキシ）、アルキ

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レンオキシ置換アルコキシ基（例えばエチレンオキシエトキシ）を表す。

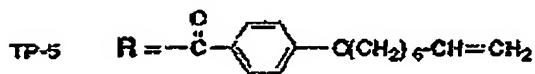
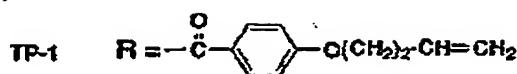
【0059】式中、トリフェニレン環に結合する6つのベンゾイルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一つは置換基P1を有する。6つの $R^{11}$ は各自独立にアルコキシ基（例えばエトキシ、プロポキシ、ブトキシ、ベンチルオキシ、ヘキシルオキシ、ヘブチルオキシ）、置換アルコキシ基（例えば、エチレンオキシエトキシ）を表す。

【0060】6つの $R^{11}$ のうち少なくとも一つは末端置換基P1が置換して成るアルコキシ基であるが、P1を連結する基は、アルキレンオキシ基（例えばエチレンオキシ、ブロビレンオキシ、ブチレンオキシ、ベンチレンオキシ、ヘキシレンオキシ、ヘブチレンオキシ）、置換アルキレンオキシ基（例えばエチレンオキシエトキシ）を表す。置換基P1を有する側鎖は多いほど好ましい。但し、末端置換基P1が直接芳香環に結合してもよい。

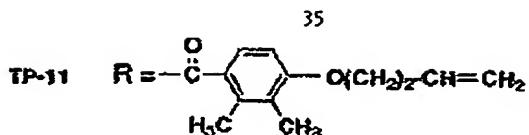
【0061】以下に、一般式(2)で表される本発明の化合物の具体例を示すが、これによって本発明が限定されることはない。

【0062】

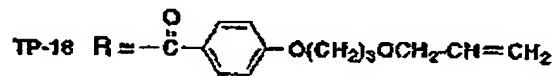
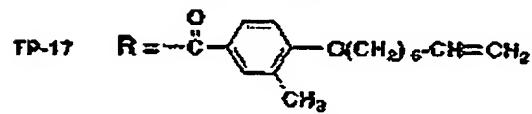
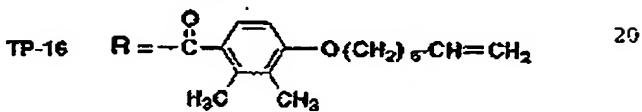
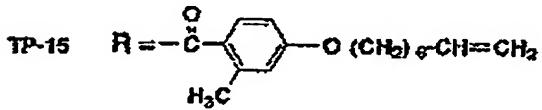
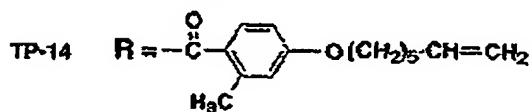
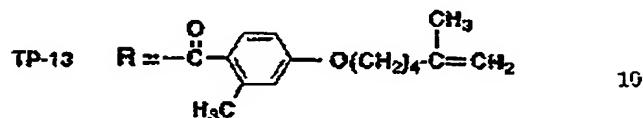
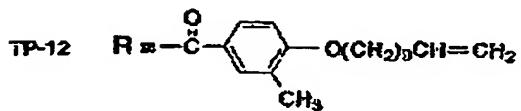
【化19】



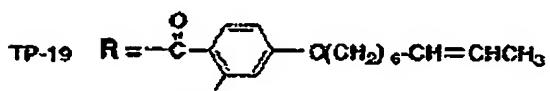
[0063]  
[化20]



[0064]  
[化21]

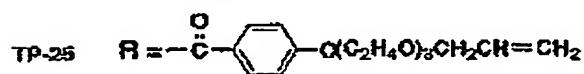
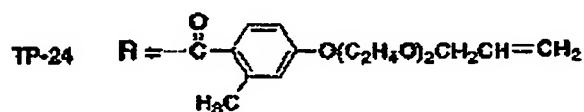
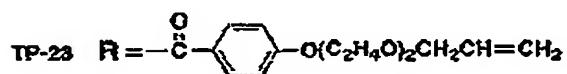
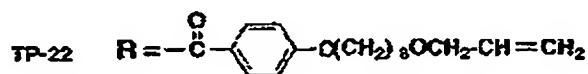
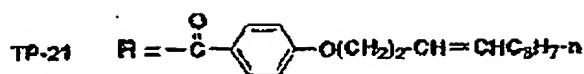


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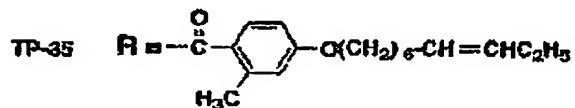
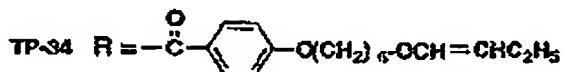
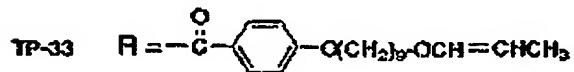
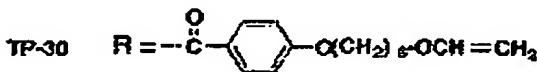
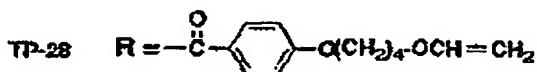
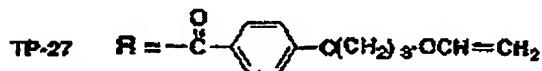
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【0065】

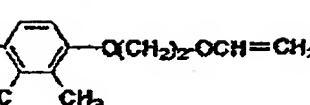
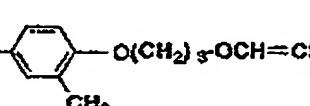
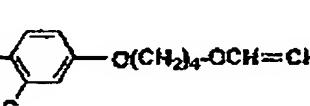
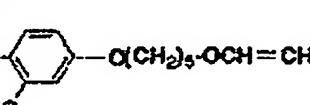
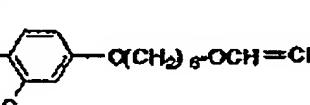
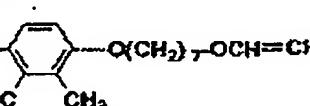
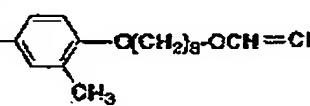
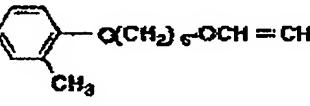
【化22】

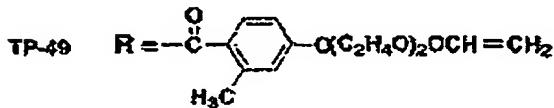
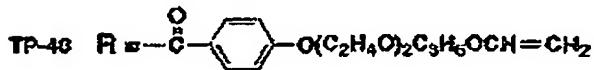
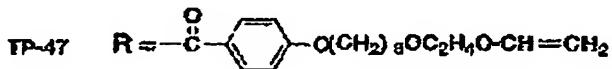
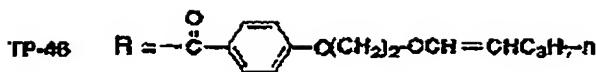


【0066】  
【化23】

(21)

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TP-36		41	[0067] [化24]
TP-37			
TP-38		10	
TP-39			
TP-40			
TP-41		20	
TP-42			
TP-43			
TP-44			
TP-45			



【0068】次に、一般式(3)について、詳細に説明する。R<sup>11</sup>、R<sup>12</sup>は、各々独立に水素原子またはメチル基を表す。R<sup>11</sup>の末端置換基P2はいわゆるアクリル基を表す。その置換基P2の置換基R<sup>11</sup>、R<sup>12</sup>は、各々独立に水素原子、アルキル基(例えばメチル、エチル、n-ブロピル、イソブロピル、n-ブチル、ベンチル、ヘキシル、ヘプチル、オクチル、ノニルが挙げられ、メチル、エチルなどの低級アルキル基が好ましく、さらにメチルが好ましい。)を表し、R<sup>11</sup>がメチルでR<sup>12</sup>が水素原子、またはR<sup>11</sup>、R<sup>12</sup>が共に水素原子の組み合わせが好ましい。

【0069】置換基R<sup>10</sup>は水素原子、置換または無置換のアルキル基(例えばメチル、エチル、n-ブロピル、イソブロピル、n-ブチル、ベンチル、ヘキシル、ヘプチル、オクチル、ノニル、2-クロロエチル、3-メトキシエチル、メトキシエトキシエチルが挙げられ、メチル、エチルなどの低級アルキル基が好ましく、さらにメチルが好ましい。)を表し、水素原子が好ましい。従つて、置換基P2としては、一般には無置換のアクリルオキシ基、メタクリルオキシ基、クロトニルオキシなどの重合活性の高い官能基が好ましく用いられる。

【0070】式中、トリフェニレン環に結合する6つのペンゾイルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一つは置換基P2を有する。6つのR<sup>11</sup>は各々独立にアルコキシ基(例えばエトキシ、プロポキシ、ブトキシ、ベンチルオキシ、ヘキシルオキシ、ヘプチルオキシ)、置換アルコキシ基(例えば、エチレンオキシエトキシ)を表す。

【0071】6つのR<sup>11</sup>のうち少なくとも一つは末端置換基P2が置換して成るアルコキシ基であるが、P2を連結する基は、アルキレンオキシ基(例えばエチレンオキシ、プロピレンオキシ、ブチレンオキシ、ベンチレンオキシ、ヘキシレンオキシ、ヘプチレンオキシ)、置換アルキレンオキシ基(例えばエチレンオキシエトキシ)を表す。置換基P2を有する側鎖は多いほど好ましい。但し、末端置換基P2が直接芳香環に結合してもよい。

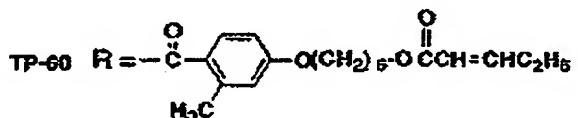
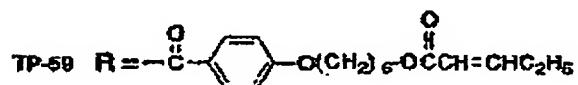
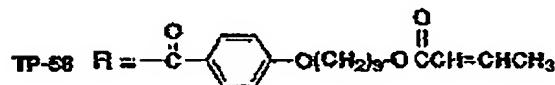
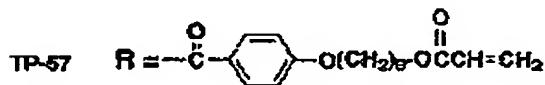
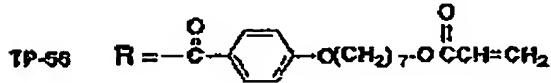
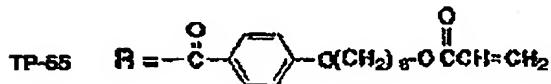
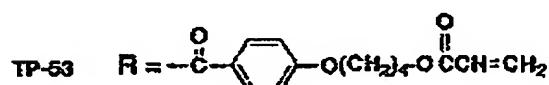
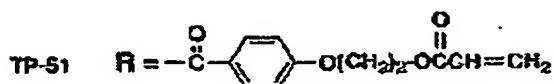
【0072】以下に、一般式(3)で表される本発明の化合物の具体例を示すが、これによって本発明が限定されることはない。

【0073】

【化25】

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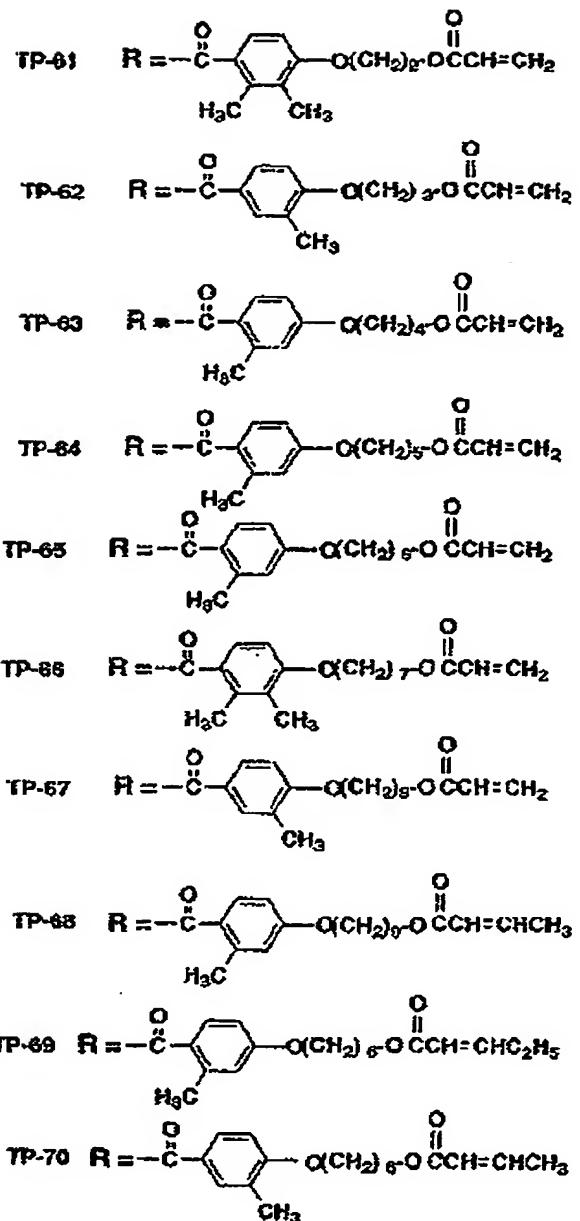


[0074]

[化26]

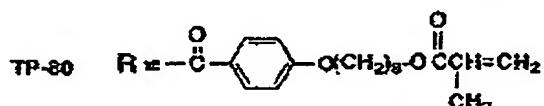
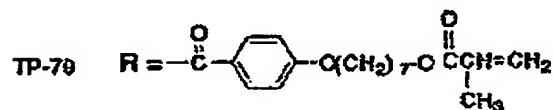
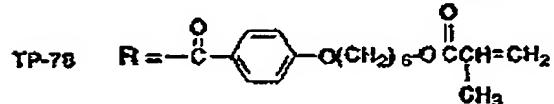
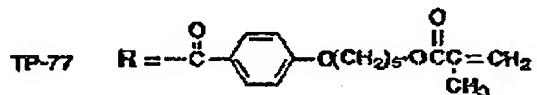
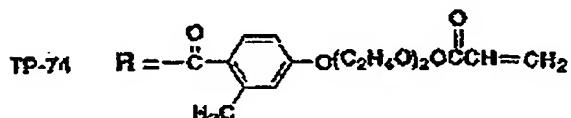
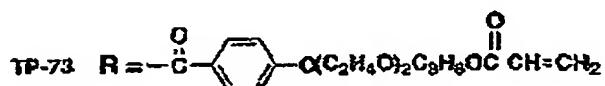
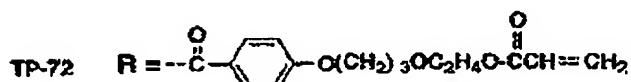
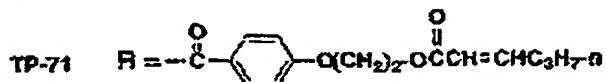
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【0075】

【化27】



【0076】次に、一般式(4)について、詳細に説明する。R'、R''は、各々独立に水素原子またはメチル基を表す。R''の末端置換基P3はいわゆるオキシラン基を表す。その置換基P3の置換基R'、R''は、各々独立に水素原子、アルキル基（例えばメチル、エチル、n-ブロビル、イソプロビル、n-ブチル、ベンチル、ヘキシル、ヘプチル、オクチル、ノニルが挙げられ、メチル、エチルなどの低級アルキル基が好ましく、さらにメチルが好ましい。）を表し、R'、R''がともに水素原子が好ましい。

【0077】置換基R'は水素原子、置換または無置換のアルキル基（例えばメチル、エチル、n-ブロビル、イソプロビル、n-ブチル、ベンチル、ヘキシル、ヘプ

チル、オクチル、ノニル、2-クロロエチル、3-メトキシエチル、メトキシエトキシエチルが挙げられ、メチル、エチルなどの低級アルキル基が好ましく、さらにメチルが好ましい。）を表し、水素原子またはメチル、エチル、n-ブロビルなどの低級アルキル基が好ましい。

【0078】式中、トリフェニレン環に結合する6つのベンゾイルオキシ基は互いに同じでも異なっていてもよいが、その内の少なくとも一つは置換基P3を有する。6つのR'は各々独立にアルコキシ基（例えばエトキシ、プロポキシ、ブトキシ、ベンチルオキシ、ヘキシルオキシ、ヘプチルオキシ）、置換アルコキシ基（例えば、エチレンオキシエトキシ）を表す。

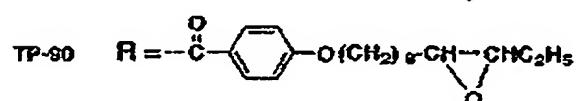
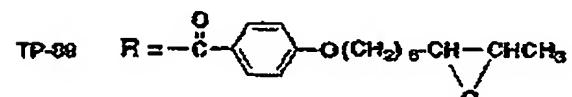
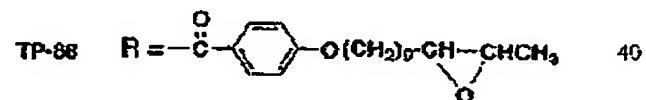
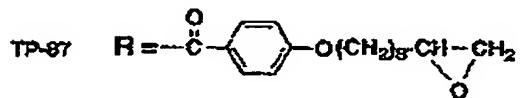
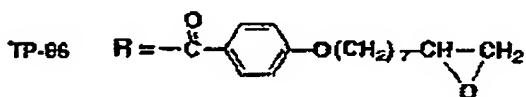
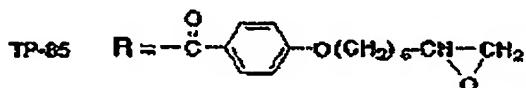
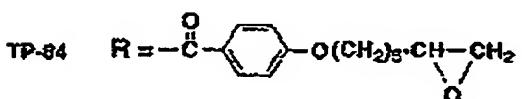
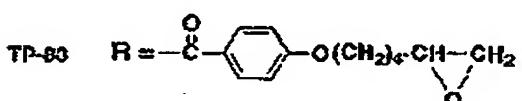
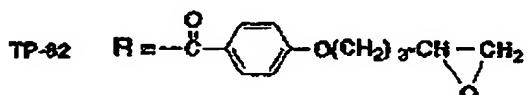
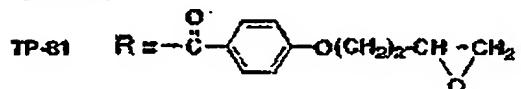
【0079】6つのR'のうち少なくとも一つは末端置

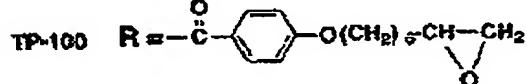
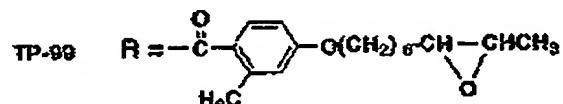
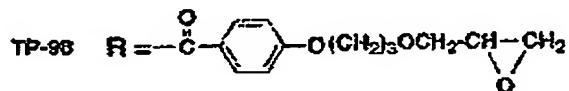
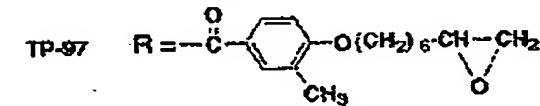
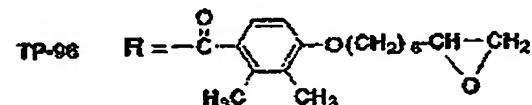
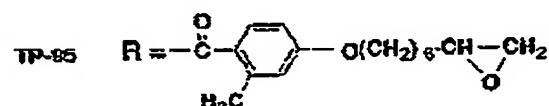
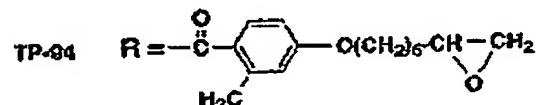
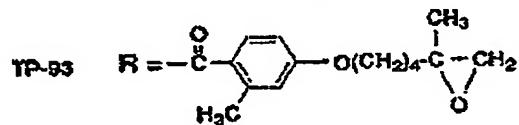
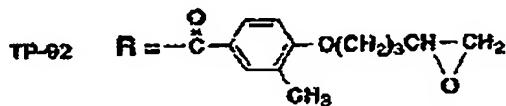
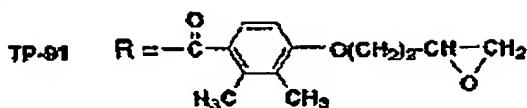
換基P3が置換して成るアルコキシ基であるが、P3を連絡する基は、アルキレンオキシ基（例えばエチレンオキシ、プロピレンオキシ、ブチレンオキシ、ベンチレンオキシ、ヘキシレンオキシ、ヘプチレンオキシ）、置換アルキレンオキシ基（例えばエチレンオキシエトキシ）を表す。置換基P3を有する側鎖は多いほど好ましい。但し、末端置換基P3が直接芳香環に結合してもよい。【0080】以下に、一般式(4)で表される本発明の化合物の具体例を示すが、これによって本発明が限定されることはない。

【0082】  
【化29】

【0081】

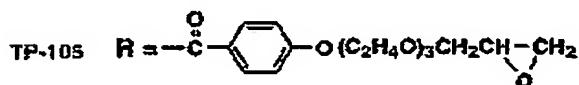
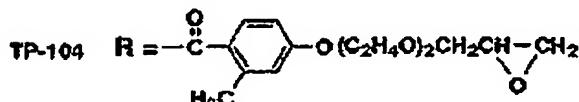
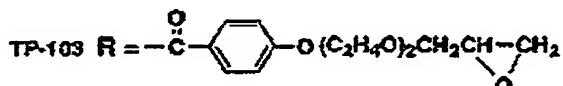
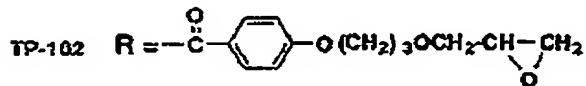
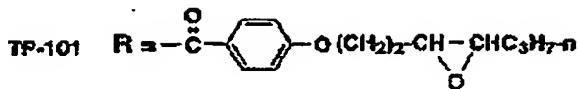
【化28】





[0083]

[1530]



【0084】本発明の液晶性化合物は単独で用いられるだけでなく、前記〔3〕、〔4〕、〔5〕に記載した組成物として、すなわち混合物としても有用な性質を發揮させうる。本発明における我々の目的は、有用な円盤状化合物の配向を維持することによる耐熱性の付与にあるが、より具体的な目的の一つは、本発明の液晶性化合物をモノドメイン性の光学的に一軸の配向状態をとらせるこにより、光学的に有意な機能を発現させ、それを光学機能素子として提供することにある。

【0085】しかし、製造段階まで含め光学機能素子に対する様々な要求を、単独の液晶で全て満足することは、必ずしも容易ではない。例えば、ある特定の好みの液晶相をとる相転移温度が高すぎて用いられる支持体の種類が限られたり、その液晶相が熱的に不安定であり耐久性が不満足であったり、光学轴の傾斜角が好みの角度でなく最良の光学特性を得られなかつたりする場合がある。そのような際に、我々は本発明の液晶性化合物、冒頭にも述べたように、似た構造にあるその他の円盤状液晶化合物、また円盤状化合物に限らず、重合性基を有する棒状ネマティック液晶性化合物あるいはコレステリック液晶性化合物を混合することによってその物性を調節できることを見出した。

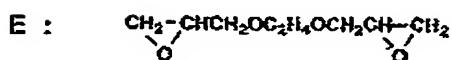
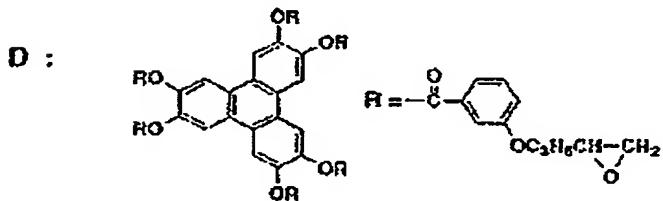
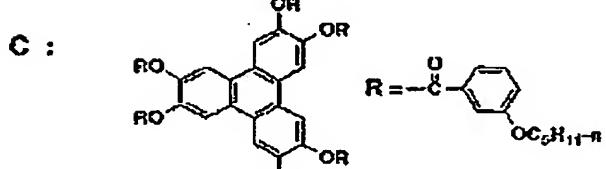
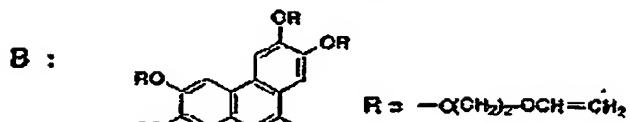
【0086】混合する化合物は、液晶性もしくは非液晶性の高分子化合物だけでなく、種々の低分子化合物も用

いられる。高分子化合物としては例えば、ポリメチルメタアクリレート、アクリル酸・メタクリル酸共重合体、スチレン・無水マレイミド共重合体、ポリビニルアルコール、N-メチロールアクリラミド、スチレン、ビニルトルエン共重合体、クロロスルホン化ポリエチレン、ニトロセルロース、ポリ塩化ビニル、塩素化ポリオレフィン、ポリエステル、ポリイミド、酢酸ビニル・塩化ビニル共重合体、エチレン・酢酸ビニル共重合体、ポリエチレン、ポリプロピレン、ポリカーボネート、シリレート系ポリマー等の液晶ポリマー等が挙げられる。

【0087】また、低分子化合物としては、重合性基を有する上記の高分子物質を形成するに用いられたモノマーが挙げられるが、P1、P2、P3を有し、本発明に含まれないトリフェニレン化合物及びP1、P2、P3を同一分子内に2つ以上有する化合物（例えばエチレングリコール-1,4-シアクリレート、エチレングリコール-1,4-シグリシジルエーテルや市販の紫外線硬化樹脂モノマー）がより好ましく用いられる。

【0088】本発明の化合物を混合することも好ましいが、以下に本発明以外で混合系に好ましく用いられる化合物の例を挙げる。

【0089】  
【化31】



【0090】一般式(2)、一般式(3)あるいは一般式(4)で表される化合物と上記の化合物との組成物における混合比は、好ましくは一般式(2)、一般式(3)あるいは一般式(4)で表される化合物の含有量として重量比50%以上、100%未満であり、さらに好ましくは60%以上、100%未満である。

【0091】本発明の該ディスコティック液晶を用いて構成される光学異方性材質は、ディスコティック液晶のみで構成されていても良いが、一般的には、支持体上に所望の光学異方性を発現した液晶層が少なくとも一層設けられたもので、用途に応じて液晶層の上下もしくは液晶層間に保護膜もしくは支持体が存在してよい。

【0092】支持体素材は光透過率が良好であることと加えて、光学的等方性に近いことが望ましい。従って、ガラスやゼオネックス(日本ゼオン)、ARTON(日本合成ゴム)、フジタック(富士フィルム)などの商品名で売られている固有複屈折値が小さい素材から形成された支持体が好ましい。しかし、ポリカーボネート、ポリアクリレート、ポリスルホン、ポリエーテルスルホン等の固有複屈折値が大きな素材であっても、製膜時に分子配向を制御することによって光学的に等方的な支持体を形成することも可能であり、それらも好適に利用される。

【0093】保護膜用素材としては、例えば、ポリメチルメタクリレート、アクリル酸・メタクリル酸共重合体、ステレン・無水マレイミド共重合体、ポリビニルアルコール、N-メチロールアクリルアミド、ステレン・ビニルトルエン共重合体、クロロスルホン化ポリエチレン、ニトロセルロース、ポリ塗化ビニル、塗素化ポリオレフィン、ポリエステル、ポリイミド、酢酸ビニル・塗化ビニル共重合体、エチレン・酢酸ビニル共重合体、ポリエチレン、ポリブロビレン、ポリカーボネート等の高分子物質；及びシランカップリング剤などの有機物質を擇ることができる。また、ω-トリコサン酸、ジオクタデシルジメチルアンモニウムクロライド及びステアリン酸メチルなどのラングミュア・プロジェクト法(LB法)により形成される脂質膜も用いることができる。

【0094】また、予め支持体上に設けられた保護膜が、配向膜として液晶層形成時の分子配向にしばしば大きな影響を与えることは、棒状液晶の場合にはよく知られた事実であり、無機または有機の配向膜としてほとんど必ず用いられている。これは、本発明でも好ましく用いられる技術の一つであり、金層斜方蒸着膜としてはSIO斜方蒸着膜が、また有機配向膜としてはラビングされたポリイミド膜が代表的なものであるが、その他ラビングした変性ポバールやラビングしたシリル化剤で処理

したガラス基板またはラピングしたセラチン膜などが用いられる。しかし、ラピングする代わりにポリビニアルコールの薄膜を4～5倍に延伸したり、特別に上記の保護膜を設けないで直接ガラス基板をラピングするなどの方法も用いることができる。

【0095】本発明の光学異方性材料を構成する該液晶層は、蒸着法やスピンドルコート、ディップコート、エクストルージョンコートなどの塗布法により支持体上の配向膜の上に設けられた薄膜として形成できる。

【0096】薄膜の膜厚は、ディスコティック液晶層の複屈折率との積が液晶セルのレターデーションに等しくなるように設定されるもので、一義的に決められないが、0.1から10μmの範囲が好ましく、1から3μmの範囲がより好ましい。

【0097】従って、少なくとも片方の界面が気相と接した状態、即ち一般的な塗布法により支持体上の配向膜の上に液晶薄膜を形成し、乾燥後、液晶層形成温度範囲内の温度で、ディスコティックネマティック層または一軸性の柱状相を形成させつつ一定時間熱処理し、そのまま続いて熱重合させるかまたは光架橋重合させた後冷却することによって所望の光学特性をもち、かつ熱的耐久性の高い光学異方性材料を得ることができる。

【0098】本発明で用いられる重合の過程は、一般に、液晶が好ましい光学異方性を示す、すなわち配向膜上で加熱によりモノドメインの一軸配向の状態になってから行われる。エポキシ基の場合は、紫外線によるカチオン型の重合も可能であるが、短時間での配向後、さらに数十度昇温し、熱重合によって固定することができる。従って、モノドメイン配向が必要ならば、ディスコティックネマティック相形成温度範囲の高い方に設定される。しかし、紫外線による光重合開始剤を用いるラジカル重合やカチオン重合は一般に極めて重合速度が大きく、製造工程では生産性的点で好ましい。

【0099】本発明における光重合開始剤としては、米国特許第2,367,661号、同第2,367,670号各明細書に記載されているα-カルボニル化合物、米国特許第2,448,828号明細書に記載されているアシロインエーテル、米国特許第2,722,512号明細書に記載されているα-炭化水素で置換された芳香族アシロイン化合物、米国特許第3,046,127号、同第2,951,758号明細書に記載されている多核キノン化合物、米国特許第3,549,367号明細書に記載しているトリアリールイミダゾールダイマー／p-アミノフェニルケトンの組み合わせ、特開昭60-105667号、米国特許第4,239,850号明細書に記載しているアクリシン及びフェナシン化合物、米国特許第4,212,970号明細書に記載しているオキサジアゾール化合物等が挙げられる。本発明の組成物中のこれらの光重合開始剤系の含有濃度は通常わずかなものであり、また不適当に多い場合には有効光

線の遮断等好ましくない結果を生じる。本発明における光重合開始剤系の量は、溶媒を除いた塗布組成物の0.01%から20%の範囲で十分であり、更に好ましくは0.5%から5%で良好な結果を得る。更に本発明では、必要により、種々の有機アミン化合物を併用することができ、それによってその効果を増大せしめることができる。これらの有機アミン化合物としては、例えばトリエタノールアミン、ジエタノールアニリン、p-ジメチルアミノ安息香酸エチルエステル、ミヒラーケトンが挙げられる。有機アミン化合物の添加量は全光重合開始剤量の50～200%が好ましい。更に本発明で用いる光重合開始剤に必要に応じてN-フェニルグリシン、2-メルカブトベンゾチアゾール、N,N-ジアルキルアミノ安息香酸アルキルエステル等の水素供与性化合物を加えることによって更に光重合開始能力を高めることができる。また、酸素による重合阻害を抑制するために、界面活性剤を少量添加することも効果的である場合が多い。

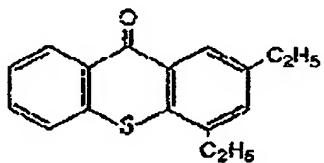
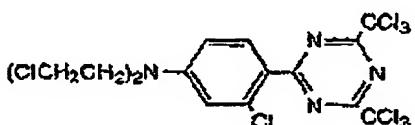
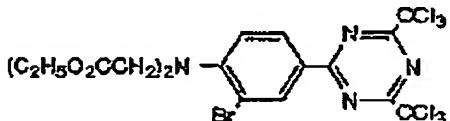
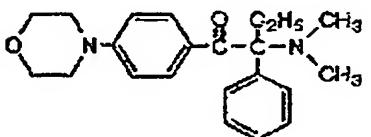
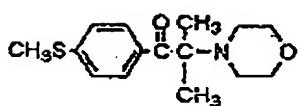
【0100】エポキシ基の重合には、紫外線活性化カチオン触媒として、アリルジアゾニウム塩（ヘキサフルオロfosfato、テトラフルオロボラート）、ジアリルヨードニウム塩、VIa族アリロニウム塩（PF<sub>6</sub>、AsF<sub>6</sub>, SbF<sub>6</sub>）のようなアニオンをもつアリルスルホニウム塩）が好ましく用いられる。

【0101】また重合用の光源としては、電子線、紫外線、可視光線、赤外線（熱線）を必要に応じて用いる事ができるが、一般的には、紫外線が用いられる。その光源としては、低圧水銀ランプ（殺菌ランプ、螢光ケミカルランプ、ブラックライト）、高圧放電ランプ（高圧水銀ランプ、メタルハライドランプ）、ショートアーク放電ランプ（超高圧水銀ランプ、キセノンランプ、水銀キセノンランプ）が挙げられる。高圧水銀灯の場合、一般的に20mJから5000mJの照射エネルギーが用いられ、好ましくは100mJから800mJである。

【0102】本発明のベンゾイルオキシトリフェニレン環化合物の場合は、一般的に～270nmに入射光を有し、その分子吸光係数も大きいため、254nmなどの短波の紫外線は有効には用いられない場合がある。従って、光重合開始剤も下記の近紫外に吸収帯を持つ化合物が好ましく用いられ、光源も高圧水銀ランプやメタルハライドランプなど近紫外光を強く放射できるものが好ましく用いられる。

【0103】

【化32】



【0104】以下、図面を用いてTN型液晶表示素子を例にとり本発明の光学異方性材料すなわち液晶表示素子用位相差膜の作用を説明する。図1、図2は、液晶セルにしきい電圧以上に十分な電圧を印加した場合の液晶セル中を伝搬する光の偏光状態を示したものである。コントラストの視野角特性には、特に電圧印加時の光の透過率特性が大きく寄与するため、電圧印加時を例にとり説明する。図1は、液晶セルに光が垂直に入射した場合の偏光状態を示した図である。自然光 $\text{I}_1$ が偏光板PAをもつ偏光板Aに垂直に入射したとき、偏光板PAを透過した光は、直線偏光 $\text{L}_1$ となる。

【0105】TN型液晶セルに十分な電圧を印加した時の液晶分子の配列状態を、概略的に一つの液晶分子でモデル的に示すと、概略図中LCのようになる。液晶セルTN-C中の液晶分子LCの分子長軸が光の道筋と平行な場合、入射面（光の道筋に垂直な面内）での屈折率の差が生じないので、液晶セル中を伝搬する常光と異常光の位相差は生じず液晶セルを通過した直線偏光は液晶セルを透過しても直線偏光のまま伝搬する。偏光板Bの偏光軸PBを偏光板Aの偏光軸PAと垂直に設定すると、液晶セルを透過し他直線偏光 $\text{L}_2$ は偏光板Bを透過することができず、暗状態となる。

【0106】図2は、液晶セルに光が斜めに入射した場

- 合の光の偏光状態を示した図である。入射光の自然光 $\text{I}_1$ が斜めに入射した場合、偏光板Aを透過した偏光 $\text{L}_1$ はほぼ直線偏光になる（実際の場合、偏光板の特性により梢円偏光になる）。この場合、液晶の屈折率異方性により液晶セルの入射面において屈折率の差が生じ、液晶セルを透過する光 $\text{L}_2$ は梢円偏光しており偏光板Bでは完全に遮断されない。このように、斜方入射においては暗状態での光の遮断が不十分となり、コントラストの大幅な低下を招き、好ましくない。
- 10 【0107】本発明は、この様な斜方入射におけるコントラストの低下を防ぎ、視角特性を改善しようとするものである。図3に本発明による構成の一例を示した。偏光板Bと液晶セルとの間に、液晶セルの法線方向から傾いた光学鏡をもつ光学異方性材料RFが配置されている。この光学異方性材料RFは光学軸に対して光が入射する角度が大きくなる程大きく偏光する複屈折体である。この様な構成の液晶表示素子に図2の場合と同様に光が斜方入射し液晶セルを透過した梢円偏光 $\text{L}_2$ は、光学異方性材料RFを透過する時の位相遅延作用によって梢円偏光がもとの直線偏光に変調され、種々の斜方入射においても同一な透過率が得られる視角依存性のない良好な液晶表示素子が実現できた。

- 【0108】本発明によって、液晶表示素子の視野角を大幅に向上できることについては以下のように推定している。TN-LCDの多くは、ノーマリーホワイトモードが採用されている。このモードでは、視野角を大きくすることに伴って、黒表示部からの光の透過率が著しく増大し、結果としてコントラストの急激な低下を招いていることになる。黒表示は電圧印加時の状態であるが、この時には、TN型液晶セルは、光学軸が、セルの表面に対する法線方向から若干傾いた正の一軸性光学異方体とみなすことができる。また、中間階調の場合には、その光学鏡は更に液晶セルの法線方向から傾いていくものと思われる。

- 【0109】液晶セルの光学鏡が液晶セルの表面に対する法線方向から傾いている場合、光学軸が法線方向にある光学異方体では、その補償が不十分であることが予想される。また、液晶セルが正の一軸性光学異方体と見なせるのであれば、それを補償するためには負の一軸性光学異方性シートは、光学鏡が法線方向から傾いた負の一軸性光学異方体とみなすことができ、それによって大幅な視野角特性が改善されたものと推定する。

- 【0110】本発明における負の一軸性とは、光学異方性を有するシートの3軸方向屈折率を、その値が小さい順に $n\alpha$ 、 $n\beta$ 、 $n\gamma$ としたとき、 $n\alpha < n\beta = n\gamma$ の関係を有するものである。従って光学軸方向の屈折率が最も小さいという特性を有するものである。但し $n\beta$ と $n\gamma$ の値は厳密に等しい必要はなく、ほぼ等しければ十分である。具体的には、 $n\beta - n\gamma / n\beta - n\alpha$

くり、2であれば实用上問題ない。また、TFT、TN型液晶セルの視野角特性を大幅に改善する条件としては、光学轴はシート面の法線方向から5度～60度傾いていることが好ましく、10度～40度がより好ましく、20度～40度が最も好ましい。更に、シートの厚さを $D$ とした時、 $100 < (n\beta - n\alpha) \times D < 300$  nmの条件を満足することが望ましい。

## 【0111】

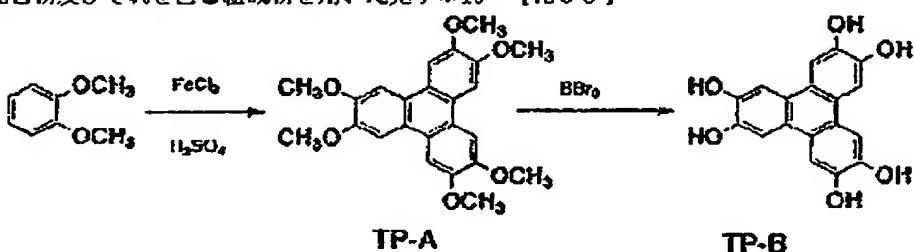
【実施例】以下に、本発明に用いられる液晶化合物の合成例、該液晶化合物及びそれを含む組成物を用いた光学\*10

\*異方性材料の作成例及びその性能の評価例を記載する。

【0112】本発明の液晶化合物は、一般に下記の経路で合成した。すなわち、1、2-ジメトキシベンゼンを出発原料としたヘキサヒドロキシトリフェニレンの合成と側鎖置換基の酸塩化物あるいは混合酸無水物の合成及びそれらの縮合であり、本実施例ではヘキサヒドロキシトリフェニレンと本発明のTP-5、TP-29、TP-55、TP-85の合成経路を下記に示す。

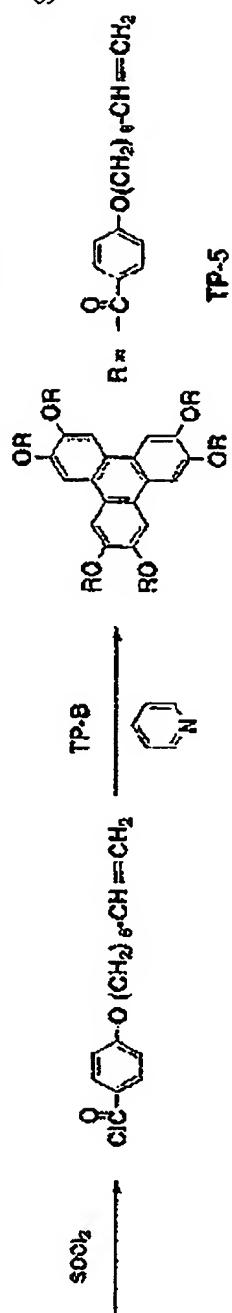
## 【0113】

## 【化33】



## 【0114】

## 【化34】

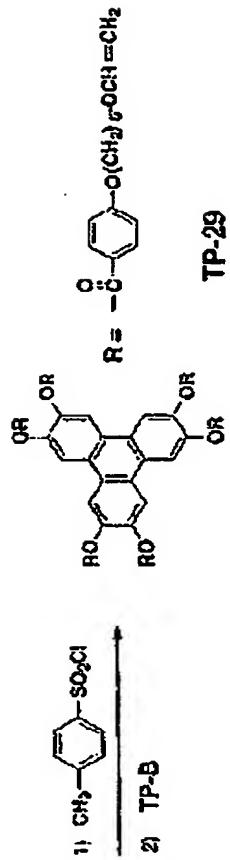


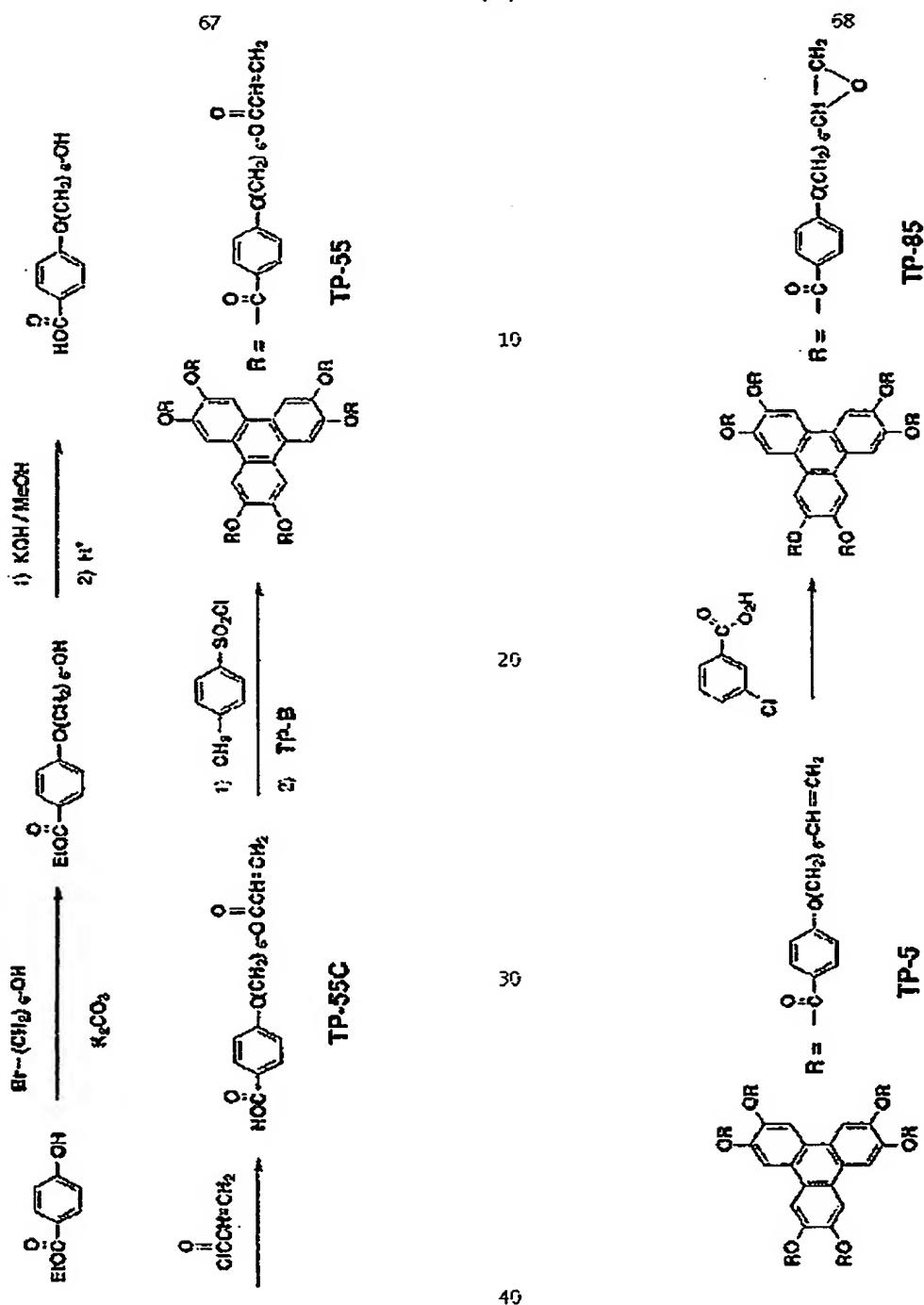
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【0115】  
【化35】【0116】  
【化36】



【0117】  
【化37】

【0118】(液晶化合物の合成)  
TP-Aの合成  
2, 3, 6, 7, 10, 11-ヘキサメトキシトリフェニレン(TP-A)の合成  
氷冷した2Lの三つ口フラスコに、硫酸第二鉄の6水塩を455gと温水193mLを入れ、メカニカルスタラーで激しく攪拌し、完全に溶解させた後、1, 2-ジメトキシベンゼンを58.7gを添加した。次に氷冷下、濃硫酸882mLを徐々に添加した。24時間後、冰水9L中に徐々に注ぎ、5時間後、反応混合物をグラスフ

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ィルターで通過し、TP-Aの粗結晶48.1g(83%)を得た。

#### TP-Bの合成

##### 2, 3, 6, 7, 10, 11-ヘキサヒドロキシトリフェニレン(TP-B)の合成

48.1gのTP-Aを850mLのジクロロメタン中に懸濁させ、三臭化ホウ素150gを徐々に添加した。2時間後、冰水7L中に注ぎ、セライト通過を行った。セライトを含む目的物を取り出し、メタノールに再溶解させ、通過した後、その滤液を減圧濃縮した。得られた残渣を減圧通過し、アセトニトリルとジクロロメタンの混合溶媒で洗浄し、目的物32.7g(86%)を得た。

#### TP-5の合成

##### 4-(7-オクテニルオキシ)-安息香酸(TP-5C)の合成

500mLの三口フラスコに、P-ヒドロキシ安息香酸33.2g、8-ブロモ-1-オクテン57.3g、炭酸カリウム41.5g及びN,N-ジメチルアセトアミド200mLを入れ、120°Cで5時間攪拌した。冷却後、反応混合物を水200mLに注ぎ、500mLの酢酸エチルで抽出し、水1000mLで2回洗浄した。無水硫酸マグネシウムで乾燥後、通過を行った。滤液を減圧濃縮後、メタノール100mLに溶解し、水酸化カリウム16.8gのメタノール溶液20mLを徐々に滴下し、2時間加熱還流した。冷却後、生じた結晶を減圧通過し、水で洗浄した。乾燥後、TP-5Cを63.3g(85%)得た。

##### 2, 3, 6, 7, 10, 11-ヘキサ(4-(7-オクテニルオキシ)ベンゾイルオキシ)トリフェニレン(TP-5)の合成

100mLの三口フラスコに4.5gのTP-5Cと5mLの塩化チオニルを入れ、2時間加熱還流した。反応終了後、過剰の塩化チオニルを減圧下留去した。これに、0.7gのTP-Bと20mLのビリシンを添加し、室温で4時間攪拌した。減圧下、過剰のビリシンを留去後、シリカゲルクロマトグラフィーを用いて精製し、TP-5を2.73g(75%)得た。

#### TP-5の同定データ

IR (cm<sup>-1</sup>) : 3080, 2940, 2860, 1740, 1605, 1580, 1510, 1470

1420, 1315, 1250, 1170, 1120, 1070, 1010, 900, 840, 760, 695  
DSC及び偏光頭微鏡観察による相転移温度測定

結晶相-132°C-D、液晶相-143°C-N、液相-227°C-等方性液体

#### [0119] TP-29の合成

##### 4-(5-ビニルオキシベンチルオキシ)安息香酸(TP-29C)の合成

500mLの三口フラスコに、P-ヒドロキシ安息香酸エチル33.2g、5-ブロモベンチルビニルエーテル

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58.0g、炭酸カリウム41.5g及びN,N-ジメチルアセトアミド200mLを入れ、120°Cで5時間攪拌した。冷却後、反応混合物を水200mLに注ぎ、500mLの酢酸エチルで抽出し、水1000mLで2回洗浄した。無水硫酸マグネシウムで乾燥後ろ過を行った。滤液を減圧濃縮後、メタノール100mLに溶解し、水酸化カリウム16.8gのメタノール溶液20mLを徐々に滴下し2時間加熱還流した。冷却後、生じた結晶を減圧ろ過し、結晶を水1Lに溶解した。濃塩酸25.7mLを加え、析出した結晶を減圧ろ過し、水で洗浄した。乾燥後、4-(5-ビニルオキシベンチルオキシ)安息香酸を64.3g(TP-29C)(90%)を得た。

#### [0120] 2, 3, 6, 7, 10, 11-ヘキサ(4-(5-ビニルオキシベンチルオキシ)ベンゾイルオキシ)トリフェニレン(TP-29)の合成

300mLの三口フラスコに、5.72gのTP-29C、トリエチルアミン6.7mL、1.2ジメトキシエタン60mLを入れ、0°Cでメタヌルホン酸クロリド2.75gをゆっくり滴下しそのまま2時間攪拌した。室温にもどし、4-ジメチルアミノビリシン0.3g、TP-B 0.65gを加え6時間攪拌した。反応混合物をろ過し、滤液を減圧濃縮後、シリカゲルカラムクロマトグラフィーを用いて精製しTP-29を2.8g(82%)得た。

#### TP-29の同定データ

IR (cm<sup>-1</sup>) : 2960, 2955, 2880, 1765, 1690, 1625, 1605, 1520, 1495, 1480, 1435  
1420, 1375, 1360, 1290, 1260, 1220, 1195, 1140, 1110, 1080, 1050, 1030, 880, 810, 780, 740

#### [0121] TP-55の合成

##### 4-(6-アクリロイルオキシヘキシルオキシ)安息香酸(TP-55C)の合成

500mLの三口フラスコに、P-ヒドロキシ安息香酸エチル33.2g、6-ブロモヘキサノール54.3g、炭酸カリウム41.5g及びN,N-ジメチルアセトアミド200mLを入れ、120°Cで5時間攪拌した。冷却後、反応混合物を水200mLに注ぎ、500mLの酢酸エチルで抽出し、水1000mLで2回洗浄した。無水硫酸マグネシウムで乾燥後ろ過を行った。滤液を減圧濃縮後、メタノール100mLに溶解し、水酸化カリウム16.8gのメタノール溶液20mLを徐々に滴下し2時間加熱還流した。冷却後、生じた結晶を減圧ろ過し、結晶を水1Lに溶解した。濃塩酸25.7mLを加え、析出した結晶を減圧ろ過し、水で洗浄した。乾燥後、4-(6-ヒドロキシヘキシルオキシ)安息香酸を61.5g(86%)得た。300mLの三口フラスコに、4-(6-ヒドロキシヘキシルオキシ)安息香酸9.53g、N,N-ジメチルアニリン5.33g、ジオキサン100mLを入れ、60°Cでアクリル酸クロリ

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F3. 9.8 gをゆっくり滴下し、6時間攪拌した。冷却後、冰水200mLに注ぎ、析出した結晶を吸引ろ過しヘキサンで洗浄、乾燥後、TP-55Cを9.4g(80%)得た。

[0122] 2, 3, 6, 7, 10, 11-ヘキサ(4-(6-アクリロイルオキシヘキシルオキシ)ベンゾイルオキシ)トリフェニレン(TP-55)の合成  
300mLの三口フラスコに、5.67gのTP-55C、トリエチルアミン6.7mL、1,2-ジメトキシエタン60mLを入れ、0°Cでメタンスルホン酸クロリド2.75gをゆっくり滴下しそのまま2時間攪拌した。室温にもどし、4-ジメチルアミノピリジン0.3g、TP-B0.65gを加え6時間攪拌した。反応混合物をろ過し、滤液を減圧濃縮後、シリカゲルカラムクロマトグラフィーを用いて精製しTP-55を3.2g(80%)得た。

[0123] TP-55の同定データ

IR (cm<sup>-1</sup>) : 2950, 2870, 1740, 1730, 1610, 1605, 1585, 1520, 1480, 1430, 1415, 1375, 1320, 1300, 1260, 1200, 1180, 1130, 1080, 1010, 990, 905, 850, 820, 760, 700

DSC及び偏光顕微鏡観察による相転移温度測定

結晶相-112°C-N。液晶相-180°C-等方性液体  
【0124】TP-85の合成

TP-85はTP-5を出発原料として合成した。  
2, 3, 6, 7, 10, 11-ヘキサ(4-(7, 8-エポキシオクチルオキシ)ベンゾイルオキシ)トリフェニレン(TP-85)の合成

100mLの三口フラスコに3.67gのTP-5とm-クロロ過安息香酸6.33g及びトルエン30mLを入れ、60°Cで2時間攪拌した。冷却後、析出したm-クロロ過安息香酸を除去し、シリカゲルクロマトグラフィーを用いて精製し、TP-85を3.17g(82%)得た。

TP-85の同定データ

IR (cm<sup>-1</sup>) : 3050, 2940, 2850, 1740, 1605, 1580, 1510, 1470, 1420, 1320, 1250, 1170, 1120, 1070, 1010, 900, 840, 760, 695

DSC及び偏光顕微鏡観察による相転移温度測定

結晶相-114°C-N。液晶相-220°C-等方性液体

【0125】実施例1(液晶化合物の光・熱重合による配向固定効果の検証)

以下、本発明の液晶化合物を含む組成物による光学異方性材料の作成法とその光・熱重合による配向固定効果について説明する。顕微鏡用スライドガラス(MATSUNAMI(株)製S-7213、サイズ7.6mm×26mm)を基板とし、液晶化合物DLC-27を10wt%の濃度でメチルエチルケトンに溶解し、その液をスピンドルコーターにより1000rpmで塗布し、ディスコティック

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ック液晶の薄膜を形成させた。これをメトラー社製FP-82 ホットステージ上で加熱し、偏光顕微鏡で相変化挙動を観察したところ、結晶相-カラムナー相を経て、147°Cで暗視野になり、等方性液体相へと転移したことがわかった。次に、液晶化合物DLC-27を10wt%の濃度でメチルエチルケトンに溶解し、さらに光重合開始剤として1wt%のヒドロキシル+ベンゾフェノン(重量比1:1)を加えた。その液をスピンドルコーターにより1000rpmでガラス基板上に塗布し、先ほどと同様にメトラー社製FP-82ホットステージ上で加熱し、偏光顕微鏡で相変化挙動を観察したところ、約110°Cでカラムナー相が安定したので、紫外線照射装置(ULTRA-VIOLET PRODUCTS社製UVSL-58(16W))を使用し、10分間光露光した。この状態では、顕微鏡視野内のカラムナー相の形態に変化は見られなかった。そこで、さらに昇温したところ、147°Cでも全く暗視野にならず、結局200°Cでも等方性液体相へと転移することはなかった。

【0126】すなわち、この事実は、円盤状化合物のDLC-27がカラムナー相という非常に秩序性の高い配向状態をとったまま、直角固定することができたことを示しており、円盤状化合物の配向を維持した薄膜状態の耐熱性向上に極めて有効な手段であることが判った。ポリエーテルカルボンの100μm厚フィルム(住友ベークライト(株)製FS-1300、サイズ100mm×100mm)を基板とし、0.1μmのゼラチン下塗り層を設け、その上に配向膜としてポリアミック酸(日産化学(株)製SE-7210)を塗布し、180°Cに焼成してポリイミド膜とした。このポリイミド膜をラビング機によりラビングして配向能を付与した。液晶組成物TP-38、TP-85、TP-85+EGDGE(重量比4:1)を10wt%の濃度で各々メチルエチルケトンに溶解し、その液をスピンドルコーターにより1000rpmで塗布し、無配向のディスコティック液晶の薄膜を形成させた。これをフィルム状物A、B、Cとした。これらを各々所定の温度で配向させ、急冷した後、各々の光軸傾斜角度β及び△n·dをエリブソメーター(AEP-100)を透過モードにしてレタデーションの角度依存性を求め、その値から最適な3軸方向屈折率と光軸の方向を計算によって求めた。

【0127】フィルム状物A

TP-38は偏光顕微鏡観察によると、約130~183°Cでディスコティックネマティック相を形成する。そこで、表面温度190°Cに加熱した金属ローラーにフィルム状物Aを支持体側から10秒間接触させ、その後、表面温度170°Cに加熱した金属ローラーに支持体側から30秒間接触させる。さらに追続して、表面温度20°Cに調整した金属ローラーに10秒間接触させることにより、本発明の光学異方性材料を得た。このシート

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を偏光顕微鏡観察したところ、モノドメインのディスコティックネマティック相をとっていることが観察された。さらにエリプソメトリーの測定によって、光軸傾斜角度 $\beta$ は35°で△n·d=125nmであった。

【0128】フィルム状物B

TP-55は偏光顕微鏡観察によると、約143°Cでディスコティックネマティック相を形成する。そこで、表面温度180°Cに加熱した金属ローラーにフィルム状物Aを支持体側から50秒間接触させ、その後、表面温度20°Cに調整した金属ローラーに10秒間接触させることにより、本発明の光学異方性材料を得た。このシートを偏光顕微鏡観察したところ、モノドメインのディスコティックネマティック相をとっていることが観察された。さらにエリプソメトリーの測定によって、光軸傾斜角度 $\beta$ は32°で△n·d=135nmであった。

【0129】フィルム状物C

TP-85は偏光顕微鏡観察によると、約171~211°Cでディスコティックネマティック相を形成する。そこで、表面温度180°Cに加熱した金属ローラーにフィルム状物Aを支持体側から50秒間接触させ、その後、表面温度20°Cに調整した金属ローラーに10秒間接触させることにより、本発明の光学異方性材料を得た。このシートを偏光顕微鏡観察したところ、モノドメインのディスコティックネマティック相をとっていることが観察された。さらにエリプソメトリーの測定によって、光軸傾斜角度 $\beta$ は70°で△n·d=155nmであった。

【0130】フィルム状物D

TP-85とEGDGEの液晶組成物は偏光顕微鏡観察によると、約109~158°Cでディスコティックネマティック相を形成する。そこで、表面温度115°Cに加熱した金属ローラーにフィルム状物Aを支持体側から30秒間接触させ、その後、表面温度20°Cに調整した金属ローラーに10秒間接触させることにより、本発明の光学異方性材料を得た。このシートを偏光顕微鏡観察したところ、モノドメインのディスコティックネマティック相をとっていることが観察された。さらにエリプソメトリーの測定によって、光軸傾斜角度 $\beta$ は44°で△n·d=120nmであった。

【0131】次に、液晶組成物TP-38、TP-55、TP-85、TP-85+EGDGE(重量比4:

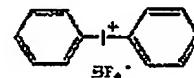
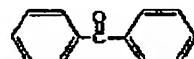
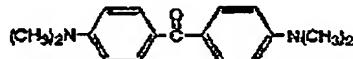
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1)の各々に光重合開始剤として1wt%のミヒラーケトン+ベンゾフェノン(重量比1:1)を加え、さらにTP-38、TP-55を除く2つの液晶組成物には1wt%のジフェニルイオドニウム・テトラフルオロボラートを加え、以後上記の方法と同様に10wt%の濃度で呑々メチルエチルケトンに溶解し、その液をスピンドルにて1000rpmで塗布し、無配向のディスコティック液晶の薄膜を形成させた。これをフィルム状物AP、BP、CP、DPとした。上記3種類の光重合開始剤の構造を下記に示す。

【0132】

【化38】



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【0133】これらを各々上記の所定の配向温度まで加熱し、1分後、紫外線照射装置(ULTRA-VIOL ET PRODUCTS社製UVSL-58(16W))を使用し、2分間光露光した後、冷却した。また上記の配向したフィルム状物Cをもう1枚同様の方法で調製し、さらに160°Cで4時間加熱処理を行い、これをフィルム状物DPHとした。上記のフィルム状物A P、BP、DP、DPH各々の光軸傾斜角度 $\beta$ 及び△n·dをエリプソメトリーで測定した後、全てのフィルム状物A、B、C、AP、BP、DP、DPHを85°Cで1000時間放置し、再度、各々の光軸傾斜角度 $\beta$ 及び△n·dをエリプソメトリーで測定した。下記の表1に、全てのフィルム状物の強制加熱前後の光軸傾斜角度 $\beta$ 、△n·d及び強制加熱前のフィルム状物のメチルエチルケトンへの溶解性を示す。

【0134】

【表1】

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表1

フィルム状物	熱測定前		熱測定後
	溶解度	光学特性 ( $\beta^*$ , $\Delta n \cdot dnm$ )	
A	○	35, 125	面状が悪化
B	○	32, 135	面状が悪化
C	○	70, 155	面状が悪化
D	○	44, 120	結晶が折出
AP	×	34, 122	35, 120
BP	×	32, 136	33, 133
CP	×	69, 148	69, 149
DP	×	41, 125	43, 125
DPH	×	43, 121	43, 121

【0135】フィルム状物Aは183°C以上で等方性液体に相転移したが、その光重合膜であるフィルム状物APは250°Cに10分以上加熱しても、その光学的異方性を維持しており、液晶性すなわち熱による相転移を示さなくなった。また、上表から明かに指摘できること20は、第一に、本発明の液晶組成物モノマーは、配向後のその温度での光・熱重合過程ではその配向を維持したまま、重合できること、第二に、重合したフィルム状物は著しく熱的耐久性が向上していることである。

実施例3 (TN型液晶表示素子の視野角拡大を目的とした位相差膜としての性能評価)

TACの127μm厚フィルム(富士タック、サイズ100mm×100mm)を基板とし、0.1μmのゼラチン下塗り層を設け、その上に配向膜として変性ポバールを塗布し、この膜をラビング機によりラビングして配向能を付与した。実施例1の表1に記載したフィルム状物CPを構成する液晶組成物を、10wt%のメチルエチルケトン溶液とし、これをスピンドルコーターにより1000rpmで塗布し、ディスコティック液晶の無配向層を形成させた。そこでフィルム状物Cと同様の方法すなわち、表面温度115°Cに加熱した金属ローラーにそのフィルム状物を支持体側から30秒間接触させ、その状態で紫外線照射装置(ULTRA-VIOLET PRODUCT社製UVSL-58(16W))を使用し、2分間光露光した後、冷却し、本発明の光学異方性材料を得た。このシートを偏光頭微鏡観察し、モノドメインの一軸配向、すなわちディスコティックネマティック相をとっていることを確認した。次に、液晶の異常光と常光の屈折率の差と液晶セルのギャップサイズの積が480nmで、ねじれ角が90度のTN型液晶セルに、上記のフィルム状物を装着し、液晶セルに対して0-5Vの30Hz矩形波におけるコントラストの角度依存性を大塚電子製LCD-5000によって測定した。コントラスト10の位置を視野角と定義し、上下左右の視野角を求めた。また、正面から見た時のコントラスト比を測定

した。ここで、上記フィルムを全く接着しないTN型液晶のみの測定値を併記した。結果を下記の表2に示す。尚、図4において矢印は位相差膜におけるラビング方向、また、液晶セルにおけるラビング方向を表している。

### 【0136】

【表2】

位相差膜	視角特性	
	上-下	右-左
有り	75~79°	82~85°
無し	23~27°	33~36°

【0137】上表から明かのように、本発明の光学信頼シートを設けたLCDにおいては、視野角特性の著しい改善が達成されている。

### 【0138】

【発明の効果】以上の実施例より、本発明の方法により得られた薄膜が熱的耐久性に優れ、モノドメイン性の優れた光学異方性シートを提供し、著しい視野角改善が可能な液晶表示素子用位相差膜を提供できることが明かである。

#### 【図面の簡単な説明】

【図1】液晶セルに光が垂直に入射した場合の光の偏光状態を示した図である。

【図2】液晶セルに光が斜めに入射した場合の光の偏光状態を示した図である。

【図3】光学異方性材料の液晶表示素子用位相差膜への使用例を示した図である。

【図4】実施例における視角特性を測定した時の偏光板の偏光軸、液晶セルのラビング方向、光学異方性シート配向膜のラビング方向の関係を示した図である。

#### 【符号の説明】

TNC: TN型液晶セル

A, B: 偏光板

PA, PB : 偏光鏡

LO : 自然光

L1, L5 : 直線偏光

L2 : 液晶セルを通った後の変調光

L3, L4 : 扇形偏光

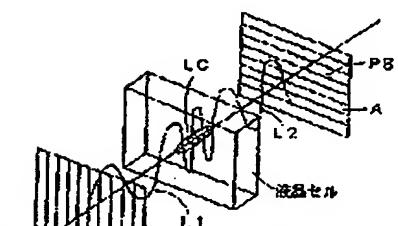
\* LC : TN型液晶セルに十分に電圧を印加した時の液晶分子の配列状態

RF1, RF2 : 液晶表示素子用位相差膜

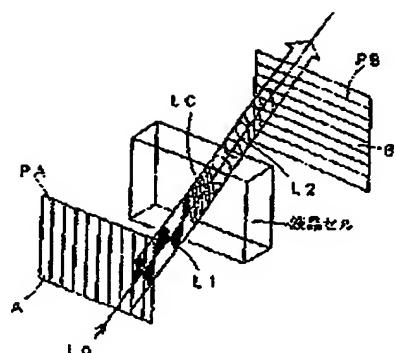
BL : バックライト

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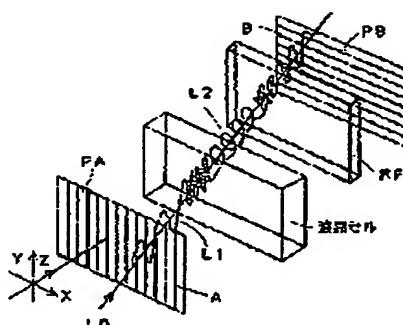
【図1】



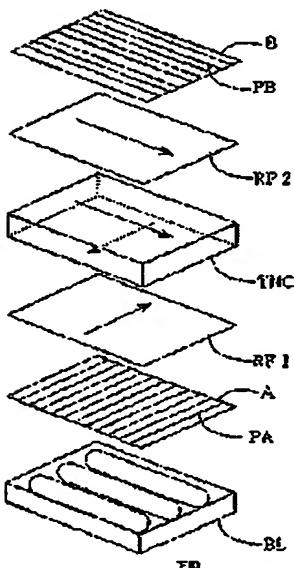
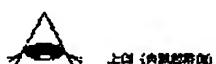
【図4】



【図2】



【図3】



フロントページの続き

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(56)参考文献 特開 平2-304526 (J.P., A)

特開 平2-111918 (JP, A)  
特開 平5-215921 (JP, A)  
特開 平2-208391 (JP, A)  
特開 平5-201142 (JP, A)  
特開 平4-113301 (JP, A)  
特開 平5-157913 (JP, A)  
特許2587398 (JP, B2)  
特許2640083 (JP, B2)  
特許2641086 (JP, B2)

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## ETAILED DESCRIPTION

### Detailed Description of the Invention]

[001]

[Industrial Application] This invention relates to the manufacture approach of a thin film useful to a liquid crystal splay, especially TN (torsion pneumatic) mold liquid crystal display.

[002]

[Description of the Prior Art] Conventionally, creation of the single crystal used for X-ray crystal structure analysis first of all is mentioned as the approach of carrying out orientation of the organic compound molecule regularly. Moreover, the approach of dipping up the Langmuir Blodgett film which developed the compound which generally has a hydrophilic part and a non-dense water space to the both ends of a molecule like a surfactant as a monomolecular layer on the water surface, and supporting on a suitable base material. Although it is structurally alike, moreover, use of the bimolecular membrane as imitation of a biomembrane, How to be used furthermore as a principle of a liquid crystal display component, make the orientation intermembrane space of two upper and lower sides impress field and electric field to an one direction and a fixed include angle spontaneously on both sides of a suitable cylindrical molecule, and carry out orientation compulsorily. Moreover, various approaches, such as an approach of arranging an alkane thiol in the front face of the vapor-deposited golden thin film, and the approach of putting in order sing the property in which the coloring matter used for the spectral sensitization for photographs meets, are mentioned.

[003] Moreover, the method of attaining the so-called glass which does not give orientation order conversely, or an MORUFOSU condition is also examined. The property of a single molecule in which it came as an object of mainly examination of the conventional chemistry is because it has many interest in a different thing which an interesting property discovers according to the aggregate structure of a molecule physically, chemically, electrically, and optically.

[004] However, most of the structure of the organic compound molecule set as the object of the approach described previously was a cylindrical molecule. This invention can say that the target disc-like molecule is the reverse structure of this cylindrical molecule in three dimensions. The structure to which the disc-like molecule used a certain atom or molecule as the core, and several side chains were extended to the radial. Or although it can classify into late-like structures which consist of large cyclic structure like crown ether and cholesterol which consists of an liphatic series carbon frame, or an aromatic series carbon frame, such as a pyrene, a naphthacene, and coronene In order that various intermolecular force, such as a pi-pi interaction, a hydrophobic interaction of an alkyl chain, and several hydrogen bond, may act two-dimensional because of the planar structure, the property by the state of ggregation is further various, and shows an interesting property.

[005] As one of the typical property of the, the liquid crystal-property originating in the above-mentioned intermolecular force of a disc-like molecule is mentioned. Although these name generically and are called a iscotheque liquid crystal compound For example, a benzene derivative, a triphenylene derivative, a torr KISEN derivative, Macro cycles, such as a phthalocyanine derivative, a cyclohexane derivative, an aza-crown system, and a phenylacetylene system, are mentioned. Although the thing of the structure where generally made these into the other nucleus of the core of a molecule, and radicals with comparatively easy composition, such as an alkyl group of straight chain, and an alkoxy group, a permutation benzyloxy radical, were permuted by the radial as the side chain is reported as what forms a liquid crystal condition There is very little knowledge about the thermal stability of the thermal behavior and liquid crystal phase.

[006] However, the property of the interesting state of aggregation also serves as the technical problem that the stability of a state of aggregation is big, in respect of the endurance, when device-izing and using the function. The optical anisotropy sheet described below is a typical example adapting the technique of this invention, and is the example which harnessed the structural description of the above-mentioned disc-like molecule, i.e., the characteristic optical function originating in the spatial electronic state resulting from both a single molecule and a state of aggregation, as an optical modulation element, and is an example which shows the importance of immobilization by the state of aggregation.

[007] CRT which is the mainstream of the display of OA equipment, such as a Japanese word processor and a desktop PC, has been changed into the liquid crystal display component with the big advantage of a thin light weight

nd a low power. Many of liquid crystal display components (Following LCD is called) which are carrying out current pread use the torsion pneumatic liquid crystal. It can divide roughly into two methods in birefringence mode and rotatory-polarization mode as the method of presentation using such liquid crystal.

008] Since 90 degrees or more of angle of torsion of liquid crystal molecular arrangement are a distorted thing and LCD using birefringence mode has a steep electro-optics property, even if there is no active element (a thin film transistor and diode), a mass display is obtained by time-sharing behavior with the electrode structure of the shape of a simple matrix. However, by the time a gradation display has the fault of being difficult and a speed of response exceeds the display engine performance of the liquid crystal display components (TFT-LCD, MIM-LCD, etc.) using an active element late (hundreds mses), it will not result.

009] 90 degrees (TN liquid crystal display device) of means of displaying in distorted rotatory-polarization mode are used for TFT-LCD or MIM-LCD for the array condition of a liquid crystal molecule. This means of displaying is most leading method as compared with LCD of other methods from monochrome display being obtained easily quickly (dozens mses), and a speed of response showing high display contrast. However, since the torsion pneumatic liquid crystal is used, by the time there is a trouble on the viewing-angle property that a foreground color and display contrast change and it exceeds the display engine performance of CRT on the principle of means of displaying according to the direction to see, it will not result.

010] The approach of expanding an angle of visibility is proposed by arranging a phase contrast film between the polarizing plate of a pair, and a TN liquid crystal cel so that JP,4-229828,A, JP,4-258923,A, etc. may see. The phase contrast film proposed in the above-mentioned patent official report will compensate the phase contrast which phase contrast discovers when phase contrast is the thing of zero mostly and it is leaned [ did not do an optical operation and ] in the perpendicular direction from the front in any way to a liquid crystal cell, and is discovered by the liquid crystal cell. However, also by these approaches, the angle of visibility of LCD is still inadequate, and the further melioration is desired. When it thinks as the object for mount, and an alternative of CRT especially, the present condition is being unable to respond at all in the present angle of visibility.

011] Moreover, although the angle of visibility is improved in JP,4-366808,A and JP,4-366809,A, using the liquid crystal cell containing the chiral pneumatic liquid crystal to which the optical axis inclined as a phase contrast film, it becomes a two-layer liquid crystal method, and cost is high and very heavy. Although the approach using the phase contrast film with which the optical axis inclines to a liquid crystal cell in JP,5-80323,A was furthermore proposed, once an optically uniaxial polycarbonate was sliced aslant and used, there was a trouble of being difficult to get, by low cost about the phase contrast film of a large area.

012] Furthermore, the approach using the phase contrast film with which the photoisomerization matter is used for a Japanese-Patent-Application-No. No. 5823 [ five to ] specification, and the optical axis inclines is indicated. According to this approach, it has a large angle-of-visibility property, and it is lightweight and the liquid crystal display component of low cost can be realized. However, there was a trouble that the stability over the heat and light of this phase contrast film was not enough as a fault of this approach.

013] Although the proposal which carries out optical compensation of LCD with the birefringent plate of the gestalt which pinched the cylindrical compound which shows liquid crystallinity to the substrate with which orientation processing of the pair was carried out in JP,5-215921,A at the time of hardening is shown, with this proposal, it is not different from the so-called double cel type proposed from the former of compensating plate at all, becomes a serious cost rise, and is not fit for mass production method as a matter of fact. As long as a cylindrical compound is furthermore used, in the birefringent plate, the angle-of-visibility improvement of the omnidirection of the TN mold LCD is impossible by the reason for optical explained later.

014] Moreover, although the proposal used as the optical compensating plate for LCD by applying a polymer liquid crystal to the film-like substrate with which the orientation film was installed is indicated, since it is impossible to carry out orientation of the molecule aslant by this approach, the angle-of-visibility improvement of the omnidirection of the TN mold LCD is impossible in JP,3-9326,A and JP,3-291601,A, too.

015] Then, this invention person is, when orientation of the discotheque liquid crystal compound is carried out with the orientation film by the Japanese-Patent-Application-No. No. 236539 [ five to ] specification, The optical axis of the thin film inclined aslant, and it was shown that it is useful as an optical compensation sheet. However, a liquid crystal display component is used as the instrument display board and the liquid crystal television for car navigation of dashboard of an automobile, and recently requires still higher thermal endurance.

016]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the manufacture approach of a thin film excellent in thermal endurance useful to a liquid crystal display, especially TN (torsion pneumatic) mold liquid crystal display.

017]

[Means for Solving the Problem] This invention uses as the thin film which heats the this applied thin film and has the molecular orientation of optical anisotropy after applying the coating liquid containing at least one sort of disc-like compounds which have the substituent which can carry out a polymerization by adding light or heat energy on this orientation film of the base material which has the orientation film on a front face and drying, and is in the manufacture approach of the thin film which consists of carrying out a polymerization and forming the thin film of

optical anisotropy by subsequently adding light or heat energy. The desirable mode of the above-mentioned manufacture approach is as follows.

The molecular orientation of optical anisotropy is a discotheque pneumatic liquid crystal layer.

A disc-like compound is a compound which is expressed with the following general formula (1) and has the actant functional group P at the end of the radial side chain.

general formula (1)

0018]

formula 5]

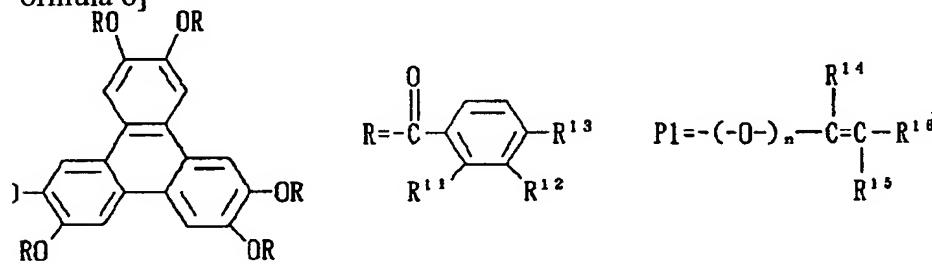
n-k-D-(L-P) k [0019] Among a formula, there is D at the core of a molecule and it expresses the radical of n organic inctions which allot a total of n substituents R and substituent - (L-P) to a radial. Respectively k P independently An ocyanate radical, a thio cyanate radical, the amino group, An alkylamino radical, an arylamino radical, a sulfhydryl group, a formyl group, An acyl group, a hydroxyl group, a carboxyl group, a sulfonic group, a phosphoryl group, a halo carbonyl group, A halo sulfonyl group, a halo phosphoryl group, an acryloyl radical, a methacryloyl radical, A totonyl radical, a vinyloxy radical, an epoxy group, an acetylenic group, a propargyl group, or an arenyl radical is expressed. (n-k) R of an individual expresses the functional group which does not contribute to formation of a polymerization constituent independently respectively, L expresses respectively the radical or chemical bond which connects P and D independently, and n expresses the integer of 3-8, and k expresses the integer of 1-n.

) A disc-like compound is expressed with a general formula (2), a following general formula (3), or a following general formula (4).

general formula (2)

0020]

formula 6]

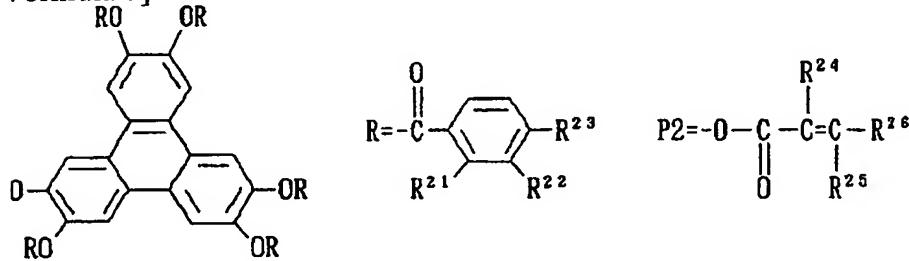


0021] although six benzoyloxy radicals combined with a triphenylene ring among a formula may differ even if they're mutually the same -- the inside of it -- a piece at least has a substituent P1. R11 and R12 express a hydrogen atom or a methyl group independently respectively, six R13 expresses an alkoxy group independently respectively, a piece at least expresses the alkoxy group containing the above-mentioned substituent P1 of them, and R14, R15, and R16 of a substituent P1 express a hydrogen atom or an alkyl group independently respectively, and n expresses 0 or 1.

general formula (3)

0022]

Formula 7]

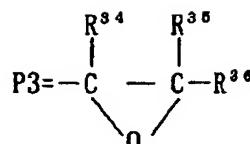
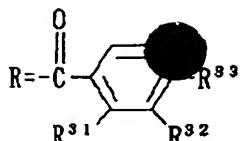
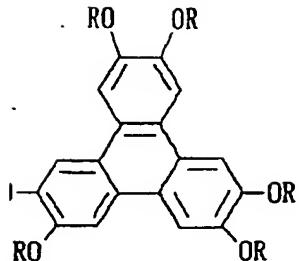


0023] although six benzoyloxy radicals combined with a triphenylene ring among a formula may differ even if they're mutually the same -- the inside of it -- a piece at least has a substituent P2. R21 and R22 express a hydrogen atom or a methyl group independently respectively, six R23 expresses an alkoxy group independently respectively, and a piece at least expresses the alkoxy group containing the above-mentioned substituent P2 of them, and R24, R25, and R26 of a substituent P2 express a hydrogen atom or an alkyl group independently respectively.

general formula (4)

0024]

Formula 8]



025] although six benzyloxy radicals combined with a triphenylene ring among a formula may differ even if they're mutually the same -- the inside of it -- a piece at least has a substituent P3. R31 and R32 express a hydrogen atom or a methyl group independently respectively, six R33 expresses an alkoxy group independently respectively, and a core at least expresses the alkoxy group containing the above-mentioned substituent P3 of them, and R34, R35, and 36 of a substituent P3 express a hydrogen atom or an alkyl group independently respectively.

026] Below, this invention is explained in detail. Although a disc-like compound is a generic name from the structural description, it can be classified into the so-called discotheque liquid crystallinity compound and non-liquid crystallinity compound which have a self-stacking tendency in physical properties. However, it is difficult to classify both physical properties from structure. What that is a disc-like compound is typical as a discotheque liquid crystal compound for example C. Destrade's and others research report, Mol.Cryst.Liq.Cryst.71 volume, The benzene derivative, triphenylene derivative which are indicated by 111 pages (1981), A torr KISEN derivative, a naphthalocyanine derivative, and B.Kohne's and others research report, Angew.Chem.96 volume, the cyclohexane derivative indicated by 70 pages (1984), and J.M.Lehn's and others research report, J. Chem.Soc.Chem.Commun., 794 pages (1985), J. Zhang's and others research report, J.Am.Chem.Soc.116 volume, The aza-crown system and phenylacetylene system macro cycle which are indicated by 2655 pages (1994) are mentioned. It is the structure where generally made these into the mother nucleus of the core of a molecule, and the alkyl group of a straight chain, an alkoxy group, a permutation benzyloxy radical, etc. were permuted by the radial as the side chain.

027] In addition, Chemical Society of Japan editing Chemistry total theory The 22nd volume, chemistry of liquid crystal The discotheque liquid crystal of the organometallic complex indicated by 135 pages (1994) is mentioned. These arrange a metal atom on the core of a molecule, and are considered that discotheque liquid crystallinity behavior shown by being located so that the ligand may surround a metal on the same flat surface.

028] On the other hand, although it is a disc-like compound, as an example of a non-liquid crystallinity compound, it is the collection II of the 69th spring annual convention lecture drafts of the Chemical Society of Japan. The cyclophane molecule of a publication etc. is mentioned to three A111, three A112, three A113, the pi electron conjugated-system molecule indicated by three A114, 1G241, 1G242, and 1G243.

029] This invention person found that it was required to control the tilt-angle distribution of a discotheque liquid crystal molecule which carried out uniaxial orientation optically adapted for the property of a liquid crystal cell, in order to study the orientation condition of the liquid crystal compound, and correspondence of an optical property in detail and to improve the display grace from all the angles of visibility of a liquid crystal cell the optimal about these disc-like compounds.

030] It is known that a discotheque liquid crystal phase can generally be divided roughly into the pillar-shaped phase (columnar phase) to which the main core of a disc-like molecule was piled up in the shape of a column by intermolecular force, the discotheque pneumatic phase which the disc-like molecule condensed confusedly, and a spiral discotheque pneumatic phase. However, W.H.de Physical written by jeu properties of liquid crystalline although a pillar-shaped phase is often found out as indicated by materials (1980 by Gordon and Breach, Science publishers), the discotheque pneumatic phase is not found out rarely.

031] Moreover, although carried out for whether being \*\* by B.Mourey's and others research report Mol.Cryst.Liq.Cryst., 84 volumes, and 193 pages (1982)], that the triphenylene system discotheque liquid crystal of this invention has a negative birefringence In order to actually apply this property as an optical compensation sheet, it required to realize the condition that the whole molecule which constitutes that thin film from on an one side base material was statistically located in a line with the one direction in the state of the room temperature. It consists of orientation fields (domain) which had specific directivity microscopically like the liquid crystal with which discotheque liquid crystal consists of the conventional cylindrical molecule generally, optical anisotropy is not shown macroscopically, and since there is a property to form the so-called multi-domain phase of light-scattering nature, when it is many, the thin film does not show the optical property that it is desirable like it can use for an optical compensation sheet.

032] Although a torr KISEN derivative, a triphenylene derivative, and a phenylacetylene system macro cycle are mentioned, especially, a triphenylene derivative is easy to compound, and when using as an optical element, it is easy to form the discotheque pneumatic phase of advantageous mono-domain nature as liquid crystal which has the property which forms a discotheque pneumatic liquid crystal phase or an optically uniaxial pillar-shaped phase among various discotheque liquid crystal about this point.

033] Generally, a triphenylene derivative points out the structure which the three more benzene rings condensed in

radical to the perimeter of the benzene ring, as shown in a general formula (2), a general formula (3), and a general formula (4), and in the liquid crystal compound reported, the compound which the alkoxy group, the alkanoloxyl radical, and the benzyloxy radical permuted at least by 2, 3, 6, 7, 10, and 11- is almost the case. And the description of this triphenylene derivative is easy to form the discotheque pneumatic phase of mono-domain nature compared with her discotheque liquid crystal. In order to be an anisotropy optically, it is necessary to lean in the direction in which optical axis is statistically, formation of the multi-domain which can also be said to be the general property of liquid crystal for that purpose is controlled, and the liquid crystal phase of mono-domain nature needs to be formed. therefore, as for the triphenylene derivative which is easy to form the discotheque pneumatic phase of mono-domain nature, the possibility as an optical different direction component is considered to be a big compound group relatively for the above-mentioned reason.

0034] As indicated on the Japanese-Patent-Application-No. No. 295501 [ five to ] specifications, this discotheque liquid crystal exists in stability by the vitreous state, maintaining that orientation condition by applying on various orientation film, such as polyimide, and carrying out orientation easily by heating beyond liquid crystal-ized temperature, and quenching in that condition. And carrying out orientation, as the discotheque liquid crystal molecule inclined uniformly in the direction of rubbing of the orientation film from measurement of the refractive-index isotropy in the condition was guessed. By the rod-like liquid crystal molecule, although an one direction can be made to carry out orientation where induction of the tilt angle is carried out in respect of each field between orientation film of two sheets like a liquid crystal cell, with discotheque liquid crystal, induction of the same tilt angle carried out on the orientation film of one \*\*. As furthermore indicated to Japanese Patent Application No. No. 0591 [ six to ], it is the big description that the tilt angle is controllable by using the discotheque liquid crystal as a principal component, and mixing another organic compound. Therefore, the discotheque liquid crystal thin film which made such and was formed is an optical anisotropy sheet in which an optical axis inclines and negative form refraction is shown clearly, and showed clearly that it is also useful as phase contrast film for liquid crystal display components.

0035] As a substituent which can carry out a polymerization, it is S.R. Sandler and W. KARO (S. R.Sandler, W.Karo) work, and organic by adding the light or heat energy of this invention, for example. Functional Group The substituent of PUREPARESHONZU (Organic Functional Group Preparations) of the 1st volume and the 2nd-volume (Academic Press, New York, and London 1968 annual publication) publication can be mentioned. Among those, they are a multiple bond, an oxirane, and an aziridine preferably. Still more preferably R.A.M.Hikmet's and others research report [Macromolecules, 25 volumes, and 4194 pages (1992)], and [Polymer, 34 volumes, No. 8, 1736 pages (1993)]. They are a double bond, i.e., an acrylic radical, a vinyl ether radical, and an epoxy group as indicated by J.Broer's and others research report [Macromolecules, 26 volumes, and 1244 pages (1993)].

0036] Generally L which connects Core D with the reactant functional group P which was indicated to the general formula (1) of the above [4] of this invention, and which contributes to a polymerization reaction has the functional group which is easy to ease the volumetric strain produced by the polymerization, for example, an alkylene group, an alkyleneoxy radical, an alkylene thio radical, an alkylene amino group, an oligo ethyleneoxy radical more desirable than a chemical bond and an oxy-radical, etc. It turns out that the orientation condition before an exposure is spoiled markedly in the polymerization process according [ the liquid crystallinity compound actually connected with the triphenylene nucleus by using a cinnamoyl radical as a photopolymerization nature machine ] to an ultraviolet radiation exposure.

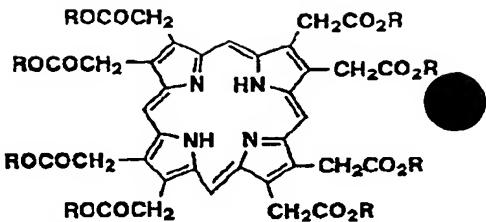
0037] On the other hand, the substituent R which does not contribute to formation of a polymerization constituent lean the radical which did not involve as a result for a polymerization reaction, and it is followed. May also include the structure of a substituent (L-P) and The similar structure, i.e., the halogen atom which generally cannot be contributed to a polymerization reaction. The alkyl group which is not permuted [ a permutation or ], an aryl group, an alkyl radical, an alkylthio group, an aryl thio radical, an arylamino radical, an alkylamino radical, an alkoxy group, an aryloxy group, and a benzyloxy radical are mentioned for a nitro group, a cyano group, an alkoxy group, etc.

0038] However, according to our examination, such high endurance is acquired in that a polymerization reaction advances on mild conditions, and it is desirable that there are many radicals which can contribute to a polymerization reaction. Moreover, it is suggested that the observed example has also remained [ the remarkable acryloyl radical ] in the polymerization constituent after sufficient polymerization reaction advances, and no reactant radicals are necessarily participating in the polymerization with the triphenylene ring compound which has an acryloyl radical in all side chains.

0039] This invention is not limited by this although the example of the compound of this invention expressed with a general formula (1) below is shown.

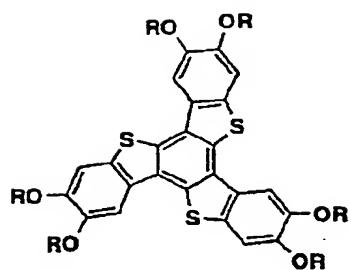
0040]

Formula 9]



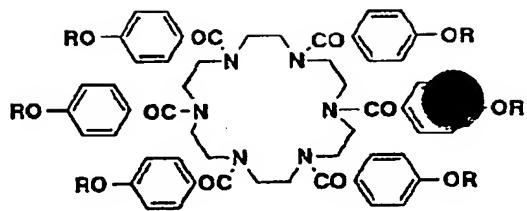
LC-NO.	R
LC-1	$-\text{C}_2\text{H}_4\text{OCOCH}=\text{CH}_2$
LC-2	$-\text{C}_4\text{H}_8\text{OCOCH}=\text{CH}_2$
LC-3	$-\text{C}_6\text{H}_{12}\text{OCOCH}=\text{CH}_2$
LC-4	$-\text{C}_9\text{H}_{16}\text{OCOCH}=\text{CH}_2$
LC-5	$-\text{C}_2\text{H}_4\text{OC}\equiv\text{CH}$
LC-6	$-\text{C}_4\text{H}_8\text{OCH}_2\text{C}\equiv\text{CH}$
LC-7	$-\text{C}_6\text{H}_{12}\text{OCH}=\text{CH}_2$
LC-8	$-\text{C}_9\text{H}_{16}\text{OCH}=\text{CH}_2$
LC-9	$-\text{C}_2\text{H}_4\text{OCH}_2\text{CH}_2\text{NH}_2$
LC-10	$-\text{C}_4\text{H}_8\text{SO}_3\text{H}$
LC-11	$-\text{C}_6\text{H}_{12}\text{OCH}_2\text{CH}-\text{CH}_2\text{O}$
LC-12	$-\text{C}_9\text{H}_{16}\text{OCH}_2\text{CH}-\text{CH}_2\text{O}$

)041]  
Formula 10]



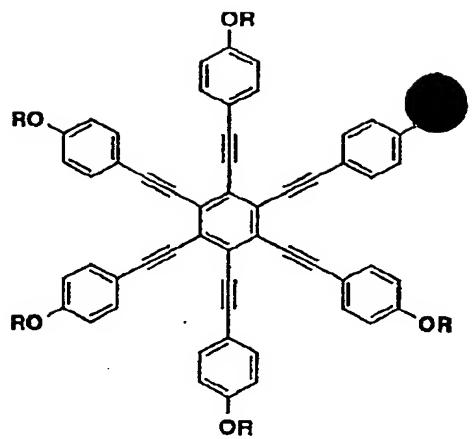
LC-NO.	R
LC-13	$\text{CH}_3$ $\text{---C}_2\text{H}_4\text{OCOC}=\text{CH}_2$
LC-14	$\text{---C}_4\text{H}_8\text{OCOCH}=\text{CH}_2$
LC-15	$\text{---C}_6\text{H}_{12}\text{OCOCH}=\text{CH}_2$
LC-16	$\text{---C}_9\text{H}_{18}\text{OCOCH}=\text{CHCH}_3$
LC-17	$\text{---C}_2\text{H}_4\text{OCH}=\text{CH}_2$
LC-18	$\text{---C}_4\text{H}_8\text{OCH}=\text{CH}_2$
LC-19	$\text{---C}_6\text{H}_{12}\text{OCONHC}_2\text{H}_4\text{NCS}$
LC-20	$\text{---C}_9\text{H}_{18}\text{OCH}=\text{CH}_2$
LC-21	$\text{---C}_2\text{H}_4\text{SC}_2\text{H}_4\text{SH}$
LC-22	$\text{---C}_4\text{H}_8\text{CHO}$
LC-23	$\text{---C}_6\text{H}_{12}\text{OCH}_2\text{CH}-\text{CH}_2$   O
LC-24	$\text{---C}_9\text{H}_{18}\text{OCH}_2\text{CH}-\text{CH}_2$   O

0042]  
Formula 11]



LC-NO.	R
LC-25	$-C_2H_4OCOCH=CH_2$
LC-26	$-C_4H_8OCOCH=CH_2$
LC-27	$-C_6H_{12}OCOCH=CH_2$
LC-28	$-C_9H_{18}OH$
LC-29	$-C_2H_4OCH=CH_2$
LC-30	$-C_4H_8CO_2H$
LC-31	$-C_6H_{12}OCH=CH_2$
LC-32	$-C_9H_{18}OCH=CH_2$
LC-33	$-C_2H_4OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$
LC-34	$-C_4H_8OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$
LC-35	$-C_6H_{12}OCH_2C\equiv CH$
LC-36	$-C_9H_{18}OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$

0043]  
Formula 12]



DLC-NO.

R

LC-37                    $-C_4H_8OCOCH=CH_2$

LC-38                    $-C_6H_{12}OCOCH=CH_2$

LC-39                    $-C_9H_{18}OCOCH=CH_2$

LC-40                    $-C_2H_4OCH=CH_2$

LC-41                    $-C_6H_{12}OCH=CH_2$

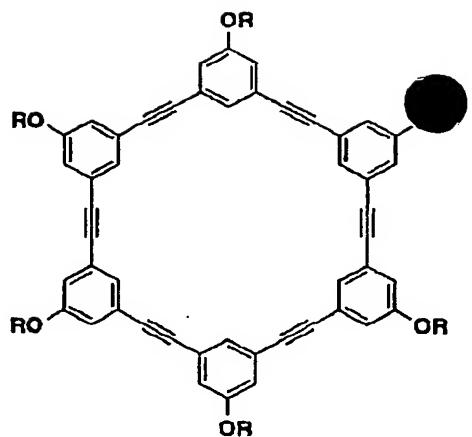
LC-42                    $-C_9H_{18}OCH=CH_2$

LC-43                    $-C_2H_4OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$

LC-44                    $-C_4H_8OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$

LC-45                    $-C_6H_{12}OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$

044]  
formula 13]



DLC-NO.

R

DLC-46                    $-C_4H_8OCOCH=CH_2$

DLC-47                    $-C_6H_{12}OCOCH=CH_2$

DLC-48                    $-C_9H_{18}OCOCH=CH_2$

DLC-49                    $-C_2H_4OCH=CH_2$

LC-50                    $-C_6H_{12}OCH=CH_2$

LC-51                    $-C_9H_{18}OCH=CH_2$

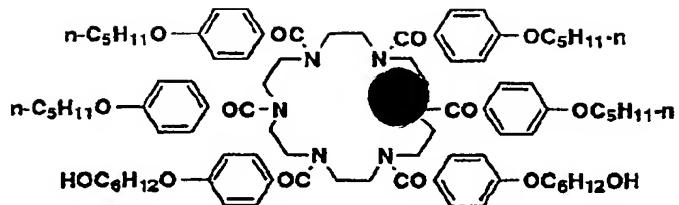
LC-52                    $-C_2H_4OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$

LC-53                    $-C_4H_8OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$

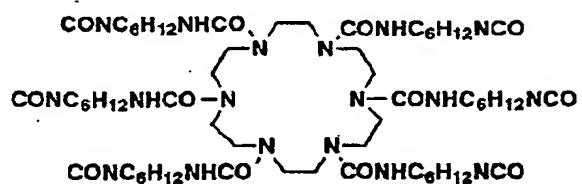
LC-54                    $-C_6H_{12}OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$

045]  
Formula 14]

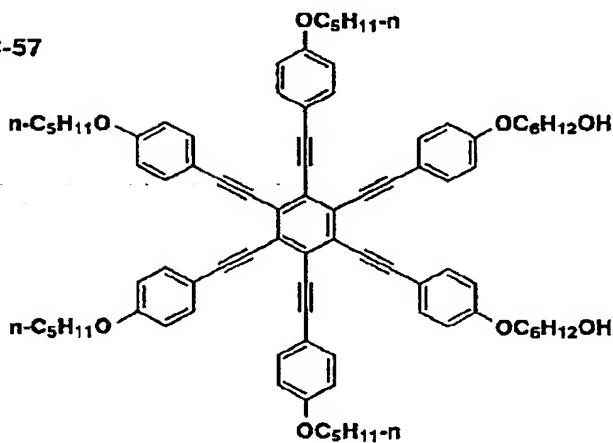
-C-55



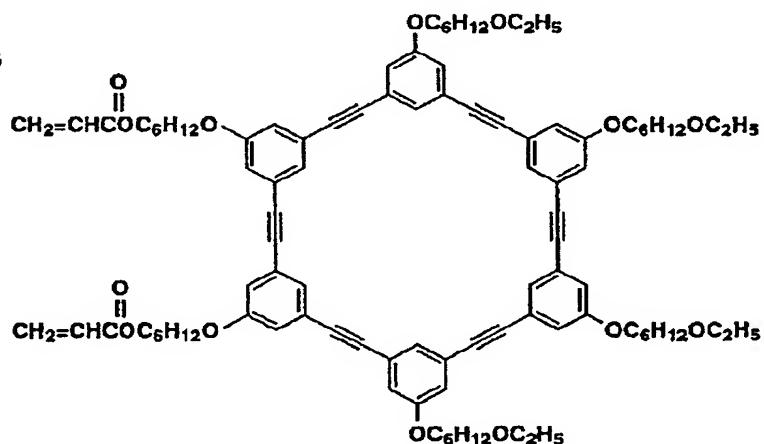
DLC-56



DLC-57

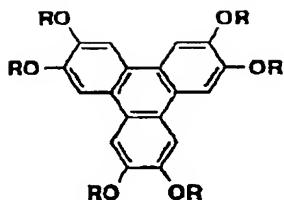


DLC-58



]046]

Formula 15]

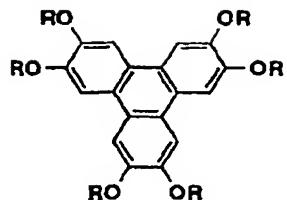


LC-NO.

R

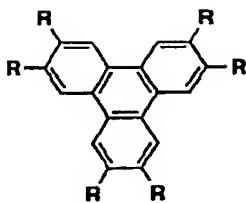
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LC-60	$-C_4H_8OCOCH=CH_2$
LC-61	$-C_6H_{12}OCOCH=CH_2$
LC-62	$-C_9H_{18}OH$
LC-63	$-C_2H_4OCH=CH_2$
LC-64	$-C_4H_8CO_2H$
LC-65	$-C_6H_{12}OCH=CH_2$
LC-66	$-C_9H_{18}OCH=CH_2$
LC-67	$-C_2H_4OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$
LC-68	$-C_4H_8OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$
LC-69	$-C_6H_{12}OCH_2C\equiv CH$
LC-70	$-C_9H_{18}OCH_2\begin{array}{c} CH \\ \backslash \\ O \\ / \\ CH_2 \end{array}$

0047]  
Formula 16]



LC-NO.	R
LC-71	$-\text{C}_2\text{H}_4\overset{\text{CH}_3}{\underset{ }{\text{OCOC}}}=\text{CH}_2$
LC-72	$-\text{C}_4\text{H}_8\text{OCOCH}=\text{CH}_2$
LC-73	$-\text{C}_6\text{H}_{12}\text{OCOCH}=\text{CH}_2$
LC-74	$-\text{C}_9\text{H}_{16}\text{OCOCH}=\text{CHCH}_3$
LC-75	$-\text{C}_2\text{H}_4\text{OCH}=\text{CH}_2$
LC-76	$-\text{C}_4\text{H}_8\text{OCH}=\text{CH}_2$
LC-77	$-\text{C}_6\text{H}_{12}\text{OCONHC}_2\text{H}_4\text{NCS}$
LC-78	$-\text{C}_9\text{H}_{16}\text{OCH}=\text{CH}_2$
LC-79	$-\text{C}_2\text{H}_4\text{SC}_2\text{H}_4\text{SH}$
LC-80	$-\text{C}_4\text{H}_8\text{CHO}$
LC-81	$-\text{C}_6\text{H}_{12}\text{OCH}_2\overset{\text{O}}{\underset{\diagdown}{\text{CH}}}-\text{CH}_2$
LC-82	$-\text{C}_9\text{H}_{16}\text{OCH}_2\overset{\text{O}}{\underset{\diagdown}{\text{CH}}}-\text{CH}_2$

)048]  
Formula 17]



DLC-NO.	R
LC-83	$\text{CH}_3$   $-\text{OC}_2\text{H}_4\text{OCOC}=\text{CH}_2$
LC-84	$-\text{OC}_5\text{H}_{10}\text{OCOCH}=\text{CH}_2$
LC-85	$-\text{NHC}_6\text{H}_{12}\text{OCOCH}=\text{CH}_2$
LC-86	$-\text{OC}_8\text{H}_{16}\text{OCOCH}=\text{CHCH}_3$
LC-87	$-\text{NHC}_2\text{H}_4\text{OCH}=\text{CH}_2$
LC-88	$-\text{OC}_3\text{H}_6\text{OCH}=\text{CH}_2$
LC-89	$-\text{OC}_6\text{H}_{12}\text{OCONHC}_2\text{H}_4\text{NCO}$
LC-90	$\text{C}_2\text{H}_5$   $-\text{OC}_2\text{H}_4\text{CHC}_3\text{H}_6\text{OCH}=\text{CH}_2$
LC-91	$-\text{SC}_2\text{H}_4\text{SC}_2\text{H}_4\text{SH}$
LC-92	$-\text{SC}_4\text{H}_8\text{CHO}$
LC-93	$-\text{SC}_6\text{H}_{12}\text{OCH}_2\text{CH}-\text{CH}_2$   O
LC-94	$-\text{SC}_9\text{H}_{18}\text{OCH}_2\text{CH}-\text{CH}_2$   O

0049] Moreover, the example of structure of the compound which is mixed with the number (DLC-No.) of the compound of this invention expressed with a general formula (1) to below, and is used for it is shown.

0050]

Formula 18]

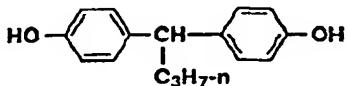
LC-NO.

## 混合物の構造

LC-9



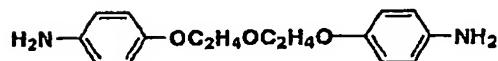
-C-11



LC-19



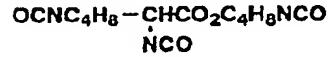
LC-22



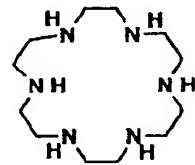
LC-28



LC-55



LC-56



0051] The compound expressed with the general formula (2), general formula (3), and general formula (4) of the above [5] of this invention has the substituent of such polymerization nature in the at least one side chain, and has a triphenylene system carbon skeletal structure at the core. The thin film has a property desirable as an optical anisotropy ingredient, and since the orientation before a polymerization is maintained, the thin film further obtained by the polymerization by light or heat is considered to be compatible in an optical property and thermal resistance.

0052] Below, a general formula (2) is explained at a detail. R11 and R12 express a hydrogen atom or a methyl group independently respectively. When n is 0, a substituent P1 expresses the double bond radical of partial saturation. The substituents R14 and R15 express a hydrogen atom and an alkyl group (for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, heptyl, octyl, and nonyl are mentioned, low-grade alkyl groups, such as methyl and ethyl, are desirable, and methyl is still more desirable.) independently respectively, and both a hydrogen atom, and R14 and R15 have [ R14 / R15 ] a combination of a hydrogen atom desirable [ the substituents ] at a methyl group.

0053] A substituent R16 expresses the alkyl group (for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, heptyl, octyl, nonyl, 2-chloro ethyl, 3-methoxy ethyl, and methoxy ethoxyethyl are mentioned, low-grade alkyl groups, such as methyl and ethyl, are desirable, and methyl is still more desirable.) which is not permuted [ a hydrogen atom, a permutation, or ], a hydrogen atom and its low-grade alkyl group are desirable, and its hydrogen atom is still more desirable.

0054] among a formula, although six benzyloxy radicals combined with a triphenylene ring may differ even if they are mutually the same, at least one of them has a substituent P1. Six R13 expresses an alkoxy group (for example, ethoxy \*\* propoxy, butoxy one, pentoxy, hexyloxy one, heptyloxy) and a permutation alkoxy group (for example, ethyleneoxy ethoxy) independently respectively.

0055] Although at least one of six R13 is the alkoxy group which the end substituent P1 permutes and changes, the radical which connects P1 expresses an alkyleneoxy radical (for example, ethyleneoxy, propyleneoxy, butylene oxy- \*\* pentene oxy- \*\* hexylene oxy- \*\* heptylene oxy-) and a permutation alkyleneoxy radical (for example, ethyleneoxy ethoxy). Much side chain which has a substituent P1 is so desirable that there is. However, the end substituent P1 may combine with a direct ring.

0056] When n is 1, the end substituent P1 of R13 the substituents R14 and R15 showing the so-called vinyl ether radical of the substituent P1 They are a hydrogen atom and an alkyl group (for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, heptyl, octyl, and nonyl are mentioned, low-grade alkyl groups, such as methyl and

hyl; are desirable, and methyl is still more desirable.) independently respectively. It expresses and both a hydrogen atom, and R14 and R15 have [ R14 / R15 ] a combination of a hydrogen atom desirable at a methyl group.

057] A substituent R16 expresses the ~~ethyl~~ group (for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, exyl, heptyl, octyl, nonyl, 2-chloro ethyl, 3-methoxy ethyl, and methoxy ethoxyethyl) are mentioned, low-grade alkyl groups, such as methyl and ethyl, are desirable, and methyl is still more desirable.) which is not permuted [ a hydrogen atom, a permutation, or ], a hydrogen atom and its low-grade alkyl group are desirable, and its hydrogen atom is still more desirable. Therefore, as a substituent P1, the vinyloxy radical which is not permuted [ which is generally a functional group with high polymerization activity ] is used preferably.

058] The alkoxy residue of which the end substituent P1 permutes and consists expresses an alkyleneoxy radical (for example, ethyleneoxy, propyleneoxy, butylene oxy-\*\* pentene oxy-\*\* hexylene oxy-\*\* heptylene oxy-) and an alkyleneoxy permutation alkoxy group (for example, ethyleneoxy ethoxy).

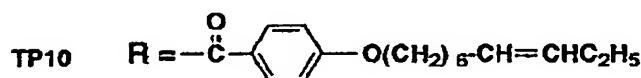
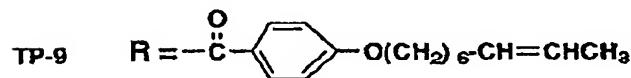
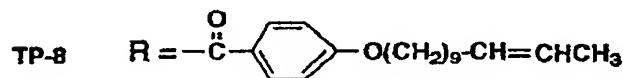
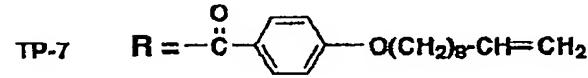
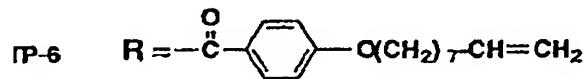
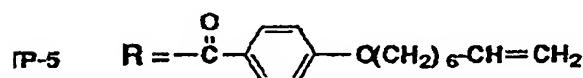
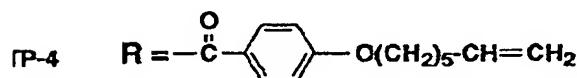
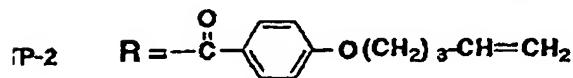
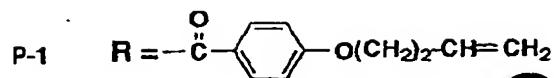
059] among a formula, although six benzyloxy radicals combined with a triphenylene ring may differ even if they are mutually the same, at least one of them has a substituent P1. Six R13 expresses an alkoxy group (for example, hydroxy \*\* propoxy, butoxy one, pentyloxy one, hexyloxy one, heptyloxy) and a permutation alkoxy group (for example, ethyleneoxy ethoxy) independently respectively.

060] Although at least one of six R13 is the alkoxy group which the end substituent P1 permutes and changes, the radical which connects P1 expresses an alkyleneoxy radical (for example, ethyleneoxy, propyleneoxy, butylene oxy-\* pentene oxy-\*\* hexylene oxy-\*\* heptylene oxy-) and a permutation alkyleneoxy radical (for example, ethyleneoxy hydroxy). Much side chain which has a substituent P1 is so desirable that there is. However, the end substituent P1 may combine with a direct ring.

061] This invention is not limited by this although the example of the compound of this invention expressed with a general formula (2) below is shown.

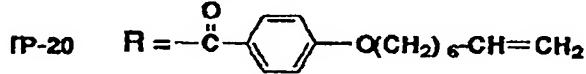
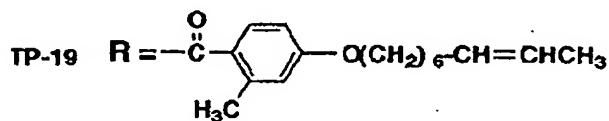
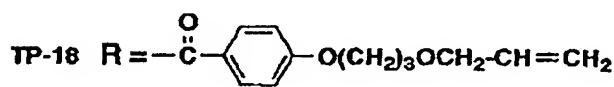
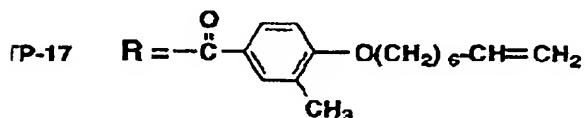
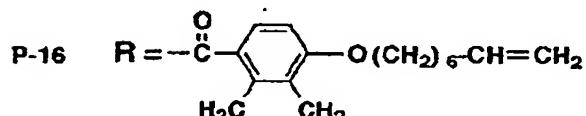
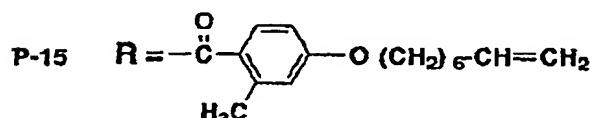
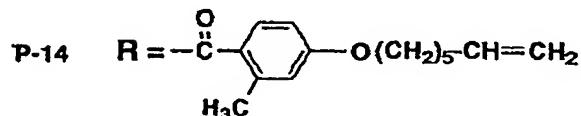
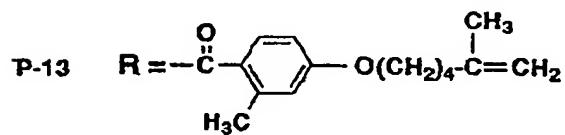
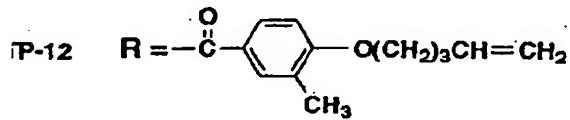
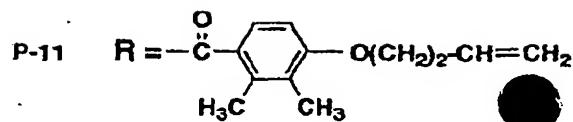
062]

Formula 19]



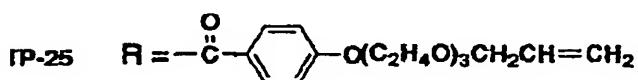
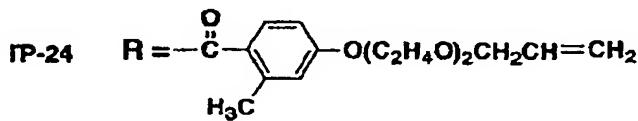
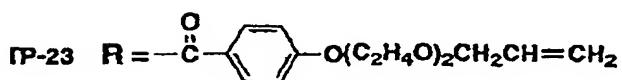
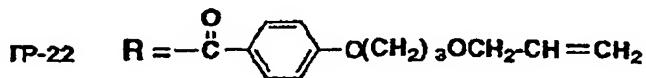
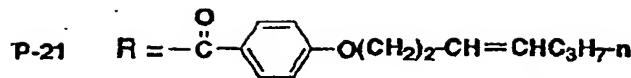
0063]

Formula 20]

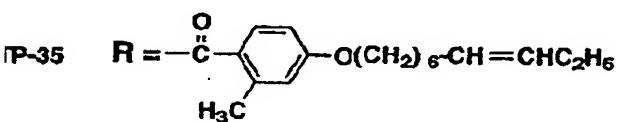
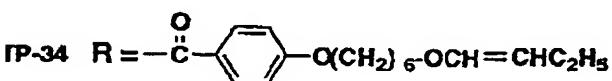
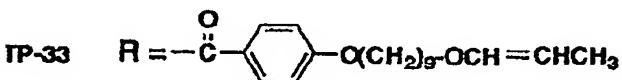
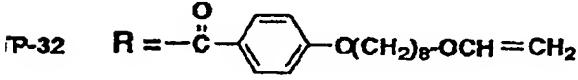
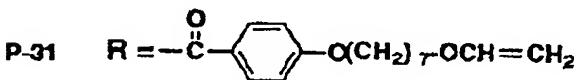
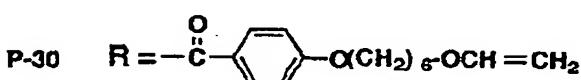
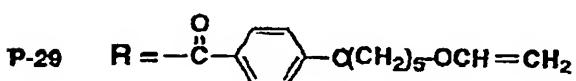
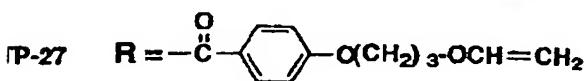
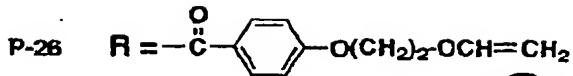


]064]

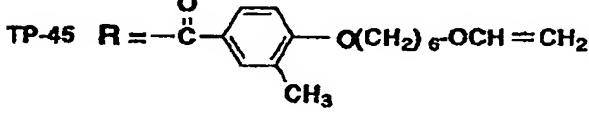
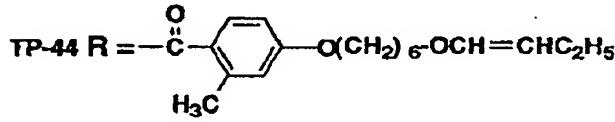
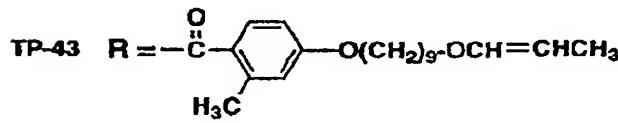
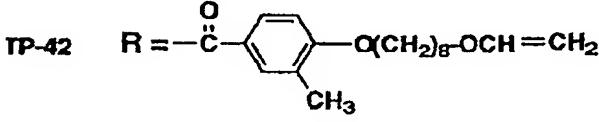
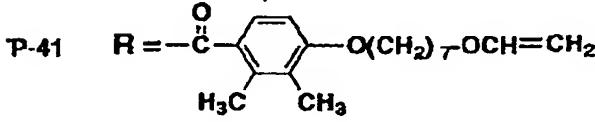
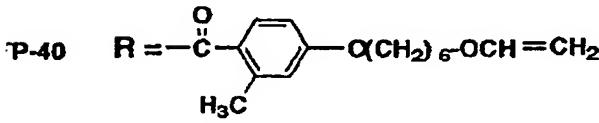
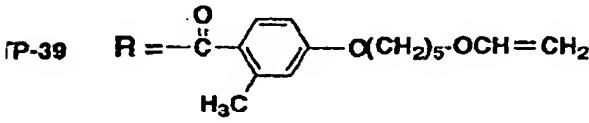
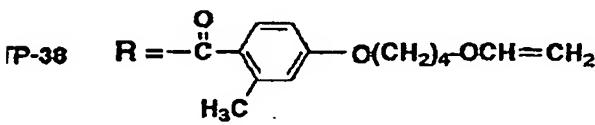
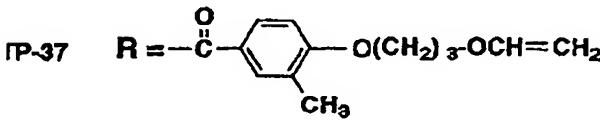
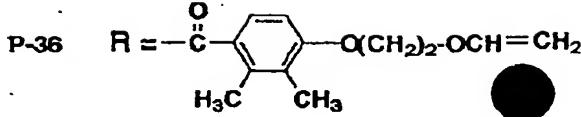
Formula 21]



065]  
formula 22]

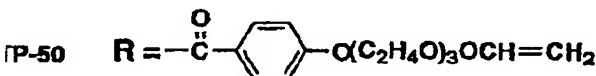
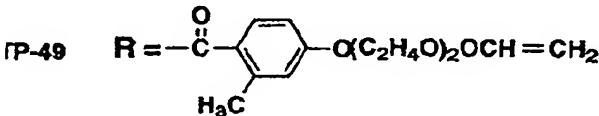
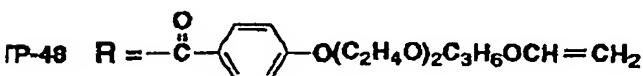
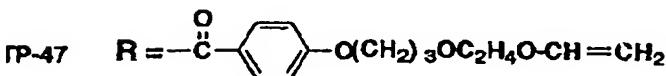
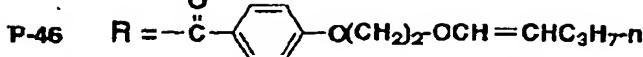


)066]  
Formula 23]



]067]

Formula 24]



]068] Next, a general formula (3) is explained to a detail. R21 and R22 express a hydrogen atom or a methyl group independently respectively. The end substituent P2 of R23 expresses the so-called acrylic radical. The substituents 24 and R25 of the substituent P2 express a hydrogen atom and an alkyl group (for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, heptyl, octyl, and nonyl are mentioned, low-grade alkyl groups, such as methyl and thyl, are desirable, and methyl is still more desirable.) independently respectively, and both a hydrogen atom, and 24 and R25 have [ R24 / R25 ] a combination of a hydrogen atom desirable [ the substituents ] at methyl.

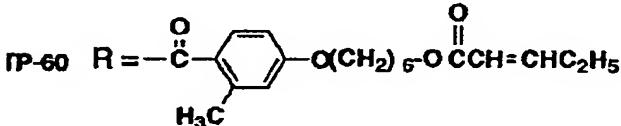
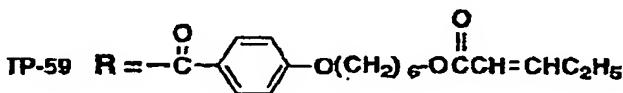
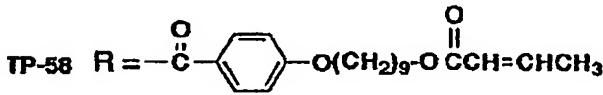
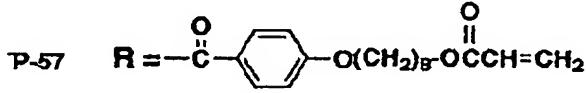
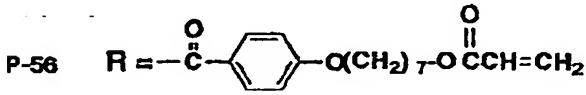
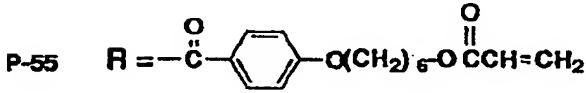
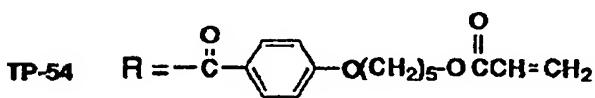
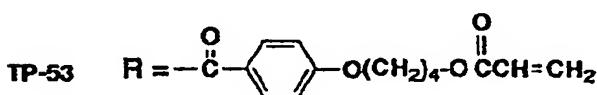
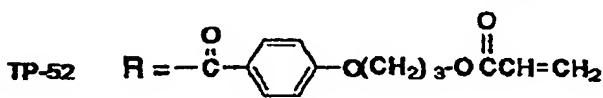
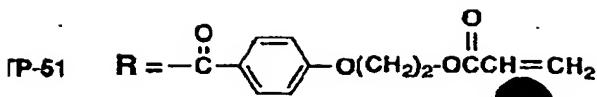
]069] A substituent R26 expresses the alkyl group (for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, exyl, heptyl, octyl, nonyl, 2-chloro ethyl, 3-methoxy ethyl, and methoxy ethoxyethyl are mentioned, low-grade alkyl groups, such as methyl and ethyl, are desirable, and methyl is still more desirable.) which is not permuted [ a hydrogen atom, a permutation, or ], and its hydrogen atom is desirable. Therefore, generally as a substituent P2, a functional group with high polymerization activity, such as a non-permuted acrylic oxy-radical, a metacryloxy radical, and UROTONIRUOKISHI, is used preferably.

]070] among a formula, although six benzyloxy radicals combined with a triphenylene ring may differ even if they're mutually the same, at least one of them has a substituent P2. Six R23 expresses an alkoxy group (for example, thoxy \*\* propoxy, butoxy one, pentyloxy one, hexyloxy one, heptyloxy) and a permutation alkoxy group (for example, ethyleneoxy ethoxy) independently respectively.

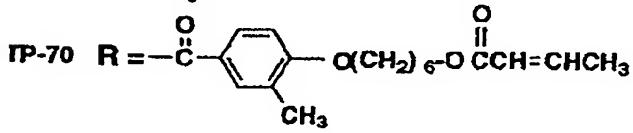
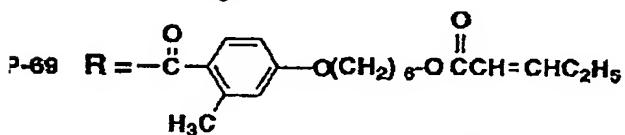
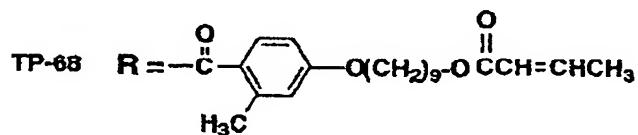
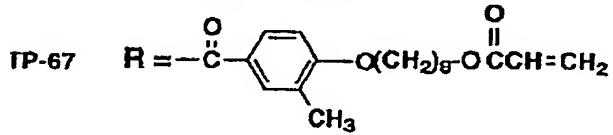
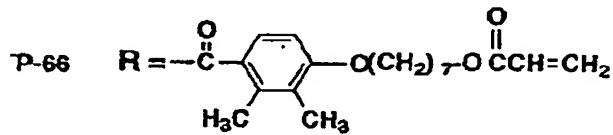
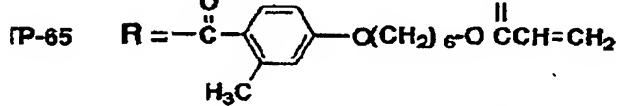
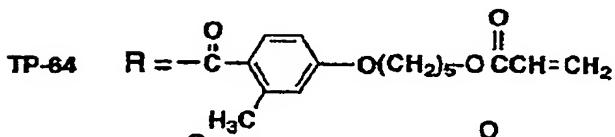
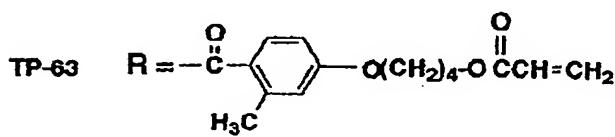
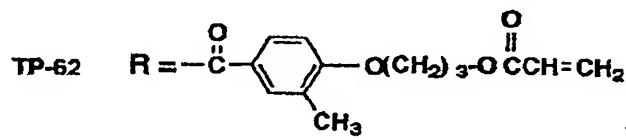
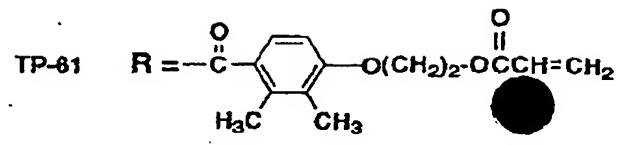
]071] Although at least one of six R23 is the alkoxy group which the end substituent P2 permutes and changes, the radical which connects P2 expresses an alkyleneoxy radical (for example, ethyleneoxy, propyleneoxy, butylene oxy- \* pentene oxy-\*\* hexylene oxy-\*\* heptylene oxy-) and a permutation alkyleneoxy radical (for example, ethyleneoxy thoxy). Much side chain which has a substituent P2 is so desirable that there is. However, the end substituent P2 may combine with a direct ring.

]072] This invention is not limited by this although the example of the compound of this invention expressed with a general formula (3) below is shown.

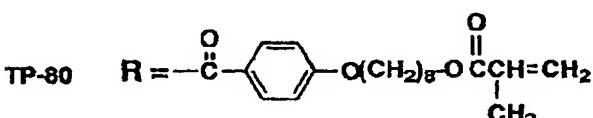
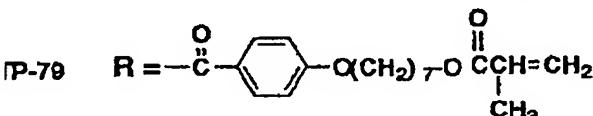
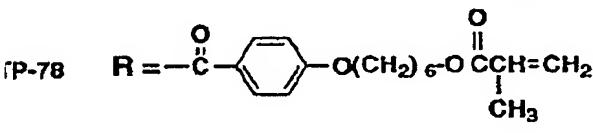
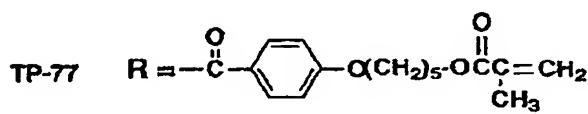
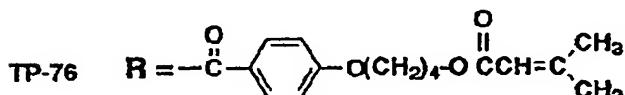
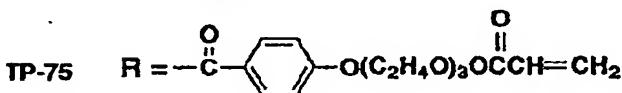
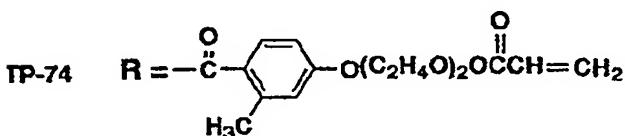
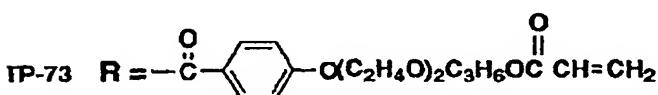
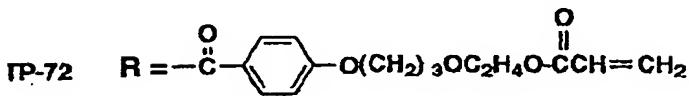
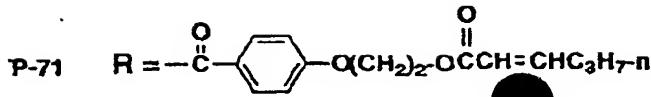
]073]  
[formula 25]



)074]  
formula 26]



[075]  
[formula 27]



)076] Next, a general formula (4) is explained to a detail. R31 and R32 express a hydrogen atom or a methyl group independently respectively. The end substituent P3 of R33 expresses the so-called oxirane radical. The substituents 34 and R35 of the substituent P3 express a hydrogen atom and an alkyl group (for example, methyl, ethyl, n-propyl, opropyl, n-butyl, pentyl, hexyl, heptyl, octyl, and nonyl are mentioned, low-grade alkyl groups, such as methyl and ethyl, are desirable, and methyl is still more desirable.) independently respectively, and both R34 and R35 are [ a hydrogen atom ] desirable.

)077] A substituent R36 expresses the alkyl group (for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, exyl, heptyl, octyl, nonyl, 2-chloro ethyl, 3-methoxy ethyl, and methoxy ethoxyethyl are mentioned, low-grade alkyl groups, such as methyl and ethyl, are desirable, and methyl is still more desirable.) which is not permuted [ a hydrogen atom, a permutation, or ], and its low-grade alkyl groups, such as a hydrogen atom or methyl, ethyl, and n-propyl, are desirable.

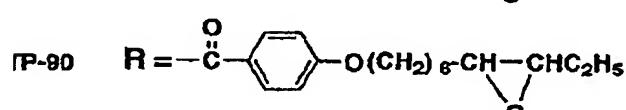
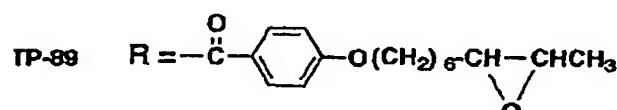
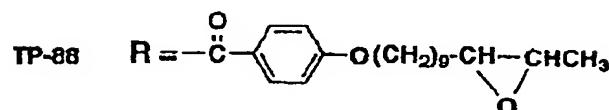
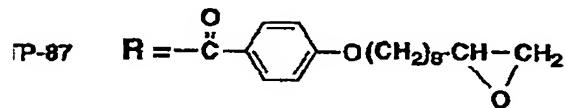
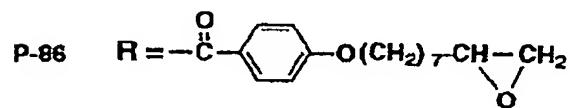
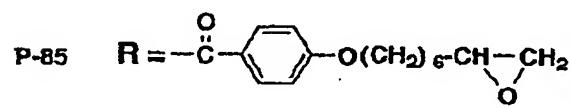
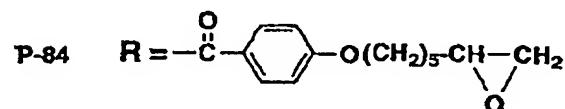
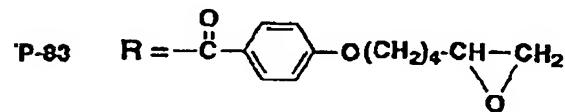
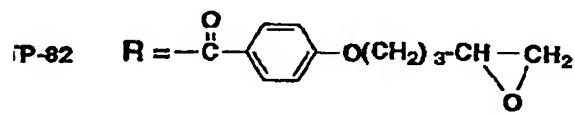
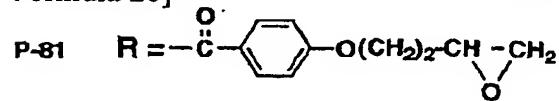
)078] among a formula, although six benzoyloxy radicals combined with a triphenylene ring may differ even if they are mutually the same, at least one of them has a substituent P3. Six R23 expresses an alkoxy group (for example, hydroxy \*\* propoxy, butoxy one, pentyloxy one, hexyloxy one, heptyloxy) and a permutation alkoxy group (for example, ethyleneoxy ethoxy) independently respectively.

)079] Although at least one of six R23 is the alkoxy group which the end substituent P3 permutes and changes, the radical which connects P3 expresses an alkyleneoxy radical (for example, ethyleneoxy, propyleneoxy, butylene oxy- \* pentene oxy-\*\* hexylene oxy-\*\* heptylene oxy-) and a permutation alkyleneoxy radical (for example, ethyleneoxy hydroxy). Much side chain which has a substituent P3 is so desirable that there is. However, the end substituent P3 may combine with a direct ring.

0080] This invention is not limited by this although the example of the compound of this invention expressed with a general formula (4) below is shown.

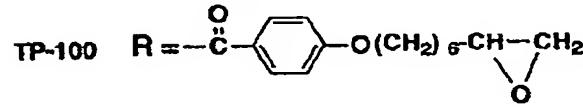
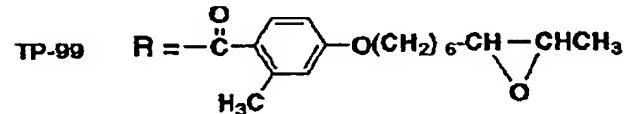
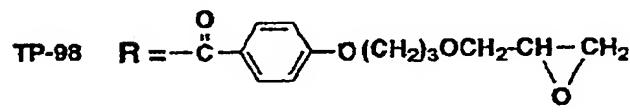
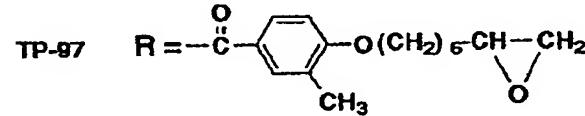
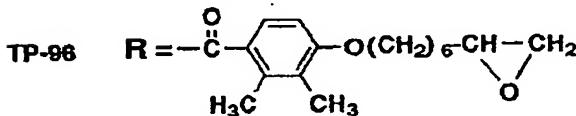
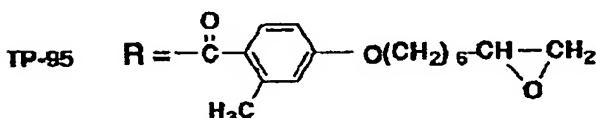
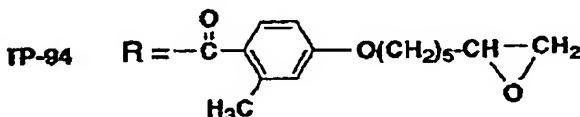
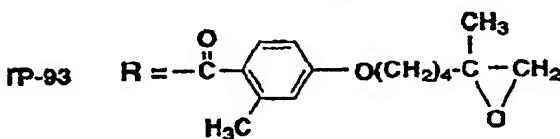
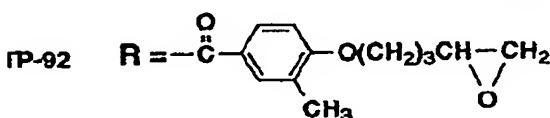
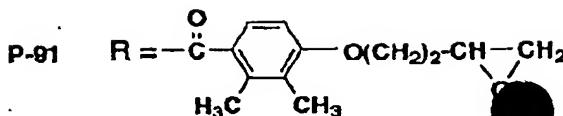
0081]

Formula 28]



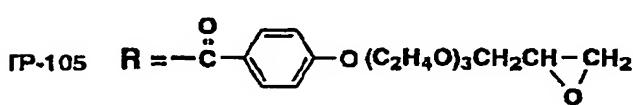
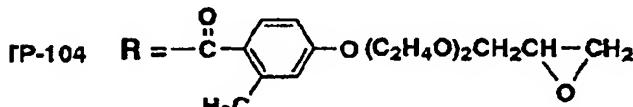
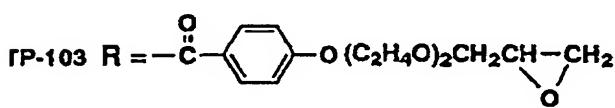
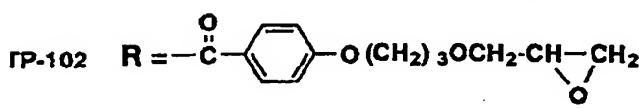
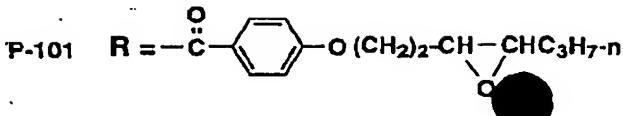
0082]

Formula 29]



]083]

Formula 30]



]084] It is not only used independently, but the liquid crystallinity compound of this invention demonstrates a property useful also as the constituent indicated to the above [3], [4], and [5], i.e., mixture, and it deals in it. Although is in the heat-resistant grant by our purpose in this invention maintaining the orientation of a useful disc-like compound, by making the liquid crystallinity compound of this invention take the orientation condition of one shaft optically [ mono-domain nature ], one of the more concrete purposes makes a significant function discover optically, and it is to offer it as an optical functional device.

]085] However, it is not necessarily easy to include to a manufacture phase and for it to be altogether satisfied with independent liquid crystal of various demands to an optical functional device. For example, the class of base material so high [ that takes the desirable liquid crystal phase of a certain specification ] and used may be restricted, or not an include angle with the thermally unstable liquid crystal phase and the tilt angle of an optical axis desirable in endurance being dissatisfied but the best optical property may not be obtained. When such, as we stated also to the liquid crystallinity compound of this invention, and the beginning, it found out that the physical properties could be adjusted by mixing the cylindrical pneumatic liquid crystal nature compound or cholesteric-liquid-crystal nature compound which has the disc-like liquid crystal compound of others in the similar structure, and not only a disc-like compound but a polymerization nature machine.

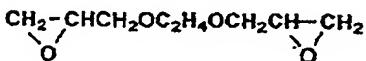
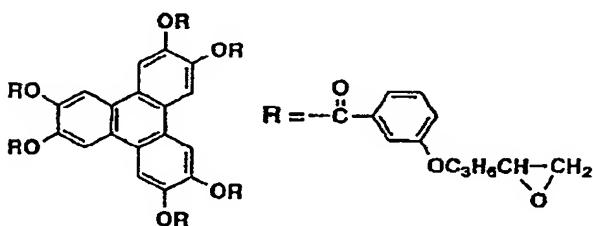
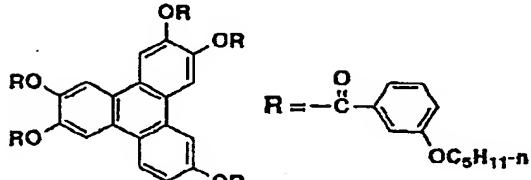
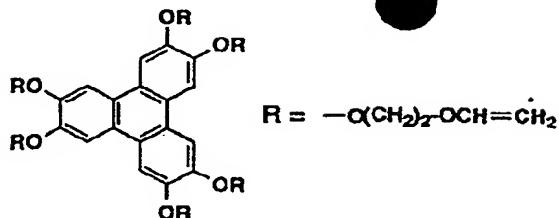
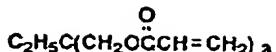
]086] The low molecular weight compound of not only the high molecular compound of liquid crystallinity or non-liquid crystallinity but versatility [ compound / to mix ] is also used. As a high molecular compound, polymethylmethacrylate, an acrylic acid and a methacrylic-acid copolymer, styrene and an anhydrous maleimide copolymer, polyvinyl alcohol, N-methylol acrylamide, styrene, a vinyltoluene copolymer, chlorosulfonated polyethylene, a nitrocellulose, a polyvinyl chloride, chlorinated polyolefins, polyester, polyimide, vinyl acetate and a vinyl chloride copolymer, an ethylene-vinylacetate copolymer, polyethylene, polypropylene, a polycarbonate, a HIRIRETO system polymer, various liquid crystal polymers, etc. are mentioned.

]087] Moreover, although the monomer used for forming the above-mentioned high polymer which has a polymerization nature machine as a low molecular weight compound is mentioned the compound (for example, ethylene glycol -1 and 4-diacrylate --) which has P1, P2, and P3, and has the triphenylene compound which is not contained in this invention, and two P1, P2 and P3 or more in the same intramolecular Ethylene glycol -1, 4-diglycidyl ether, and a commercial ultraviolet-rays hardening resin monomer are used more preferably.

]088] Although it is also desirable to mix the compound of this invention, the example of the compound preferably used for mixed stock below except this invention is given.

]089]

formula 31]



0090] as the content of the compound desirable [ in the constituent of the compound expressed with a general formula 2), a general formula (3), or a general formula (4), and the above-mentioned compound ] and expressing with a general formula (2), a general formula (3), or a general formula (4) -- a weight ratio -- it is 50% or more and less than 00%, and they are 60% or more and less than 100% still more preferably.

0091] Although the optical anisotropy ingredient constituted using this discotheque liquid crystal of this invention may consist of only discotheque liquid crystal, generally the liquid crystal layer which discovered the desired optical anisotropy was further prepared at least on the base material, and a protective coat or a base material may exist according to an application between the upper and lower sides of a liquid crystal layer, or a liquid crystal layer.

0092] As for a base material material, it is desirable that it is close to the optical isotropy in addition to light transmittance being good. Therefore, the base material formed from the material with the small proper birefringence value currently sold at trade names, such as glass, ZEONEKKUSU (Nippon Zeon), ARTON (Japan Synthetic Rubber), and FUJITAKKU (Fuji film), is desirable. However, even if it is a material with big proper birefringence values, such as a polycarbonate, polyacrylate, polysulfone, and polyether sulphone, by controlling molecular orientation at the time of film production, it is also possible to form an isotropic base material optically, and they are also used suitably.

0093] As a material for protective coats, for example Polymethylmethacrylate, an acrylic acid and a methacrylic-acid copolymer, Styrene and an anhydrous maleimide copolymer, polyvinyl alcohol, N-methylol acrylamide, A styrene inyltoluene copolymer, chlorosulfonated polyethylene, A nitrocellulose, a polyvinyl chloride, chlorinated polyolefins, polyester, Organic substances, such as high polymer [, such as polyimide, vinyl acetate and a vinyl chloride copolymer an ethylene-vinylacetate copolymer, polyethylene, polypropylene, and a polycarbonate, ]; and a lane coupling agent, can be mentioned. Moreover, the built up film formed of Langmuir-Blodgett's techniques (LB film), such as omega-tricosane acid, dioctadecyl dimethyl ammonium chloride, and methyl stearate, can also be used.

0094] Moreover, in the case of cylindrical liquid crystal, that the protective coat beforehand prepared on the base material often has big effect on the molecular orientation at the time of the liquid crystal stratification as orientation film is the fact known well, and it is almost surely used as inorganic or organic orientation film. Although this has the typical polyimide film with which it is one of the techniques in which this invention is also used preferably, and rubbing of the method vacuum evaporation film of SiO slanting was carried out as organic orientation film as method vacuum evaporation film of metal slanting again, the glass substrate processed with the denaturation poval which carried out rubbing, or the sililation reagent which carried out rubbing, or the gelatin film which carried out rubbing is used. However, approaches, such as carrying out rubbing of the direct glass substrate, can also be used without extending the thin film of polyvinyl alcohol 4 to 5 times or preparing the above-mentioned protective coat specially

instead of carrying out rubbing.

0095] This liquid crystal layer that constitutes the optical anisotropy ingredient of this invention can be formed as a thin film prepared on the orientation film on a base material by the applying method such as vacuum deposition, a spin coat, a DIP coat, and an extrusion coat. [0096] Although the thickness of a thin film is not set up so that a product with the birefringence value of a discotheque liquid crystal layer may become equal to the retardation of a liquid crystal cell, and it is not decided uniquely, its range of 0.1 to 10 micrometers is desirable, and its range of 1 to 3 micrometers is more desirable.

0097] A liquid crystal thin film is formed according to the condition to which interface of at least one of the two touched the gaseous phase, i.e., the general applying method, on the orientation film on a base material. Whenever liquid crystal layer type Nariatsu ] after desiccation therefore, at temperature within the limits or [ carrying out fixed amount heat treatment, making a discotheque pneumatic layer or an optically uniaxial pillar-shaped phase form, continuing as it is and carrying out thermal polymerization ] -- or by [ which back-cool ] having carried out the optical ridge formation polymerization, it can have a desired optical property and an optical anisotropy ingredient with high thermal endurance can be obtained.

0098] Generally, the process of a polymerization in which it is used by this invention is performed, after liquid crystal shows a desirable optical anisotropy, namely, is in the condition of the uniaxial orientation of a mono-domain with casting on the orientation film. Although the polymerization of the cation mold by ultraviolet rays is also possible, behind the orientation in a short time, the temperature up of the case of an epoxy group can be carried out further dozens times, and it can be fixed by thermal polymerization. Therefore, if mono-domain orientation is required, it will be set as the higher one of a discotheque NEMATTIKU phase formation temperature requirement. However, generally the radical polymerization and cationic polymerization using a photopolymerization initiator by ultraviolet rays have a very large rate of polymerization, and are desirable in respect of productivity in a production process.

0099] As a photopolymerization initiator in this invention, U.S. Pat. No. 2,367,661, alpha-carbonyl compound indicated by 2,367,670 each specification, The acyloin ether indicated by the U.S. Pat. No. 2,448,828 specification, the aromatic series acyloin compound permuted with alpha-hydrocarbon indicated by the U.S. Pat. No. 2,722,512 specification, U.S. Pat. No. 3,046,127, the polykaryotic quinone compound indicated by the 2,951,758 specification, the combination of the thoria reel imidazole dimer / p-aminophenyl ketone indicated by the U.S. Pat. No. 3,549,367 specification, The acridine indicated by JP,60-105667,A and the U.S. Pat. No. 4,239,850 specification and a phenazine compound, the OKISA diazole compound indicated by the U.S. Pat. No. 4,212,970 specification are mentioned. The content concentration of these photopolymerization initiator systems in the constituent of this invention is usually light, and when many [ unsuitably ], it produces results which are not desirable, such as cutoff of an effective beam of light. The amount of the photopolymerization initiator system in this invention is enough in 0.01 to 20% of range of ie spreading constituent except a solvent, and obtains a result still more desirable and good at 5% from 0.5%. Furthermore, various organic amine compounds can be used together as occasion demands, and the effectiveness can be made to increase by it in this invention. As these organic amine compounds, triethanolamine, diethanolamine, p-imethylamino ethyl benzoate ester, and a Michler's ketone are mentioned, for example. 50 - 200% of the total amount of photopolymerization initiators of the addition of an organic amine compound is desirable. Furthermore, hotopolymerization initiation capacity can be further heightened by adding hydrogen-donating-property compounds, such as N-phenylglycine, 2-mercaptopbenzothiazole, N, and N-dialkylamino benzoic-acid alkyl ester, to the hotopolymerization initiator used by this invention if needed. Moreover, in order to control the polymerization inhibition by oxygen, it is also effective to carry out little addition of the surfactant in many cases.

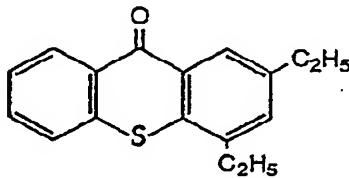
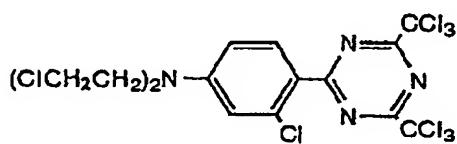
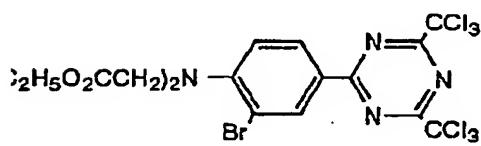
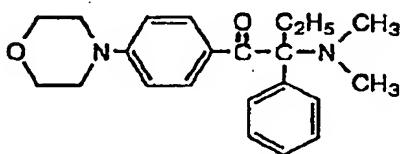
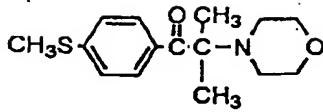
0100] Allyl compound diazonium salt (hexafluoro phosphate, tetrafluoro borate), diaryl iodonium salt, and a VIa group ant RONIUM salt (PF<sub>6</sub>, allyl compound sulfonium salt with an anion like AsF<sub>6</sub> and SbF<sub>6</sub>) are preferably used for the polymerization of an epoxy group as an ultraviolet-rays activation cation catalyst.

0101] Moreover, although an electron ray, ultraviolet rays, a visible ray, and infrared radiation (heat ray) can be used as a beam of light for polymerizations if needed, generally ultraviolet rays are used. As the light source, a low-pressure mercury lamp (a germicidal lamp, a fluorescence chemical lamp, black light), a high-pressure discharge lamp (a high-pressure mercury lamp, metal halide lamp), and a short arc discharge lamp (an extra-high pressure mercury lamp, a xenon lamp, mercury xenon lamp) are mentioned. In the case of a high pressure mercury vapor lamp, generally the exposure energy of 20mJ(s) to 5000mJ(s) is used, and they are 800mJ(s) from 100mJ(s) preferably.

0102] In the case of the benzoyloxy triphenylene ring compound of this invention, generally, it has lambdamax in -70nm, and since the molar extinction coefficient is also large, the ultraviolet rays of short wave, such as 254 etc.nm, may not be used effectively. Therefore, the compound with which a photopolymerization initiator also has an absorption band in near-ultraviolet [ following ] is used preferably, and that to which the light source can also emit strongly near-ultraviolet light, such as a high-pressure mercury lamp and a metal halide lamp, is used preferably.

0103]

Formula 32]



)104] Hereafter, taking the case of a TN liquid crystal display device, an operation of the optical anisotropy ingredient of this invention, i.e., the phase contrast film for liquid crystal display components, is explained using a drawing. Drawing 1 and drawing 2 show the polarization condition of the light which spreads the inside of the liquid crystal cell at the time of impressing sufficient electrical potential difference more than a threshold electrical potential difference to a liquid crystal cell. In order that the permeability property of the light at the time of electrical-potential-difference impression may contribute greatly especially, it explains to the angle-of-visibility property of contrast taking the case of the time of electrical-potential-difference impression. Drawing 1 is drawing having shown the polarization condition when light carries out incidence to a liquid crystal cell perpendicularly. When incidence is carried out at right angles to the polarizing plate A in which the natural light L0 has the polarization shaft PA, the light which penetrated the polarizing plate PA turns into the linearly polarized light L1.

)105] If one liquid crystal molecule shows roughly the array condition of the liquid crystal molecule when impressing sufficient electrical potential difference for a TN liquid crystal cell model, it will become like [ in / LC / schematic diagram ]. Since the difference of the refractive index in plane of incidence (inside of a field perpendicular to the course of light) does not arise when the molecule major axis of the liquid crystal molecule LC in liquid crystal cell TNC is parallel to the course of light, even if the linearly polarized light which did not produce the phase contrast of Tsunemitsu who spreads the inside of a liquid crystal cell, and abnormality light, but passed the liquid crystal cell penetrates a liquid crystal cell, it is spread with the linearly polarized light. If the polarization shaft PB of a polarizing plate B is set as the polarization shaft PA and perpendicular of a polarizing plate A, a liquid crystal cell is penetrated, and the other linearly polarized lights L2 cannot penetrate a polarizing plate B, but will be in a dark condition.

)106] Drawing 2 is drawing having shown the polarization condition of light when light carries out incidence to a liquid crystal cell aslant. When the natural light L0 of incident light carries out incidence aslant, the polarization L1 which penetrated the polarizing plate A turns into the linearly polarized light mostly (when actual, it becomes elliptically polarized light with the property of a polarizing plate). In this case, in the plane of incidence of a liquid crystal cell, the difference of a refractive index arises by the refractive-index anisotropy of liquid crystal, elliptically polarized light of the light L2 which penetrates a liquid crystal cell is carried out, and it is not completely intercepted with a polarizing plate B. Thus, in the method incidence of slanting, intercepting [ of the light in a dark condition ] becomes inadequate, the sharp fall of contrast is caused, and it is not desirable.

)107] This invention tends to prevent the fall of the contrast in such method incidence of slanting, and tends to improve a viewing-angle property. An example of the configuration by this invention was shown in drawing 3. The optical anisotropy ingredient RF with the optical axis which inclined from [ of a liquid crystal cell ] the normal between the polarizing plate B and the liquid crystal cell is arranged. This optical anisotropy ingredient RF is a

refringence object which polarizes so greatly that the include angle light carries out [ an include angle ] incidence to n optical axis becomes large. Elliptically polarized light was modulated by the linearly polarized light of a basis by the phase delayed action when penetrates the optical anisotropy ingredient RF, and elliptically polarized light L2 which light carried out method incidence of slanting to the liquid crystal display component of such a configuration like the case of drawing 2, and penetrated the liquid crystal cell has realized the good liquid crystal display component without the viewing-angle dependency from which the same permeability is obtained also in the various method incidence of slanting.

)108] By this invention, the angle of visibility of a liquid crystal display component is presumed as follows about it being improved sharply. As for many of TN-LCD, no MARI White mode is adopted. In this mode, in connection with enlarging an angle of visibility, the permeability of the light from a black display would increase remarkably, and the rapid fall of contrast will be caused as a result. Although a black display is in the condition at the time of electrical-potential-difference impression, at this time, an optical axis can consider from a normal that a TN liquid crystal cel is the forward optically uniaxial optically anisotropic body which inclined a little to the front face of a cel. Moreover, in the case of middle gradation, it is thought that the optical axis inclines from [ of a liquid crystal cell ] a normal further.

)109] When the optical axis of a liquid crystal cell leans from [ to the front face of a liquid crystal cell ] the normal, it is expected in the optically anisotropic body which has an optical axis in the direction of a normal that the compensation is insufficient. Moreover, if a liquid crystal cell can regard it as a forward optically uniaxial optically anisotropic body, in order to compensate it, a negative optically uniaxial optically anisotropic body is desirable. Since is such, it can consider that the optical anisotropy sheet in this invention is the negative optically uniaxial optically anisotropic body to which the optical axis inclined from the normal, and it is presumed to be that by which the large angle-of-visibility property has been improved by it.

)110] Optically uniaxial [ in this invention / negative ] has the relation of  $n_{\alpha} < n_{\beta} = n_{\gamma}$ , when 3 shaft-orientations refractive index of the sheet which has an optical anisotropy is set to  $n_{\alpha}$ ,  $n_{\beta}$ , and  $n_{\gamma}$  at order with the small value. Therefore, it has the property that the refractive index of the direction of an optical axis is the smallest. However, if  $n_{\beta}$  and the value of  $n_{\gamma}$  do not need to be strictly equal and are almost equal, they are enough. On a concrete target  $n_{\beta}-n_{\gamma} / n_{\beta}-n_{\alpha}$  If it is  $<0.2$ , it is satisfactory practically. Moreover, as conditions which improve sharply the angle-of-visibility property of TFT and a TN liquid crystal cel, as for an optical axis, it is desirable to lean 5 times to 60 degrees from [ of a sheet surface ] a normal, it is more desirable, and is the most desirable. [ of 20 - 40 degrees ] [ of ten - 40 degrees ] Furthermore, when thickness of a sheet is set to D, it is desirable to satisfy  $100 < (n_{\beta}-n_{\alpha}) \times D < 300$  nm conditions.

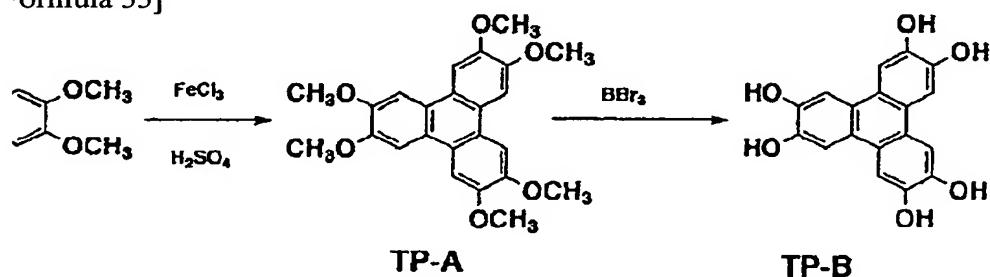
)111]

Example] The example of creation of the optical anisotropy ingredient using the constituent which contains in below the synthetic example of the liquid crystal compound used for this invention, this liquid crystal compound, and it, and the example of evaluation of the engine performance are indicated.

)112] Generally the liquid crystal compound of this invention was compounded in the following path. That is, it is composition and those condensation of composition of the hexa hydroxy triphenylene which used 1 and 2-methoxybenzene as the start raw material, the acid chloride of a side-chain substituent, or a mixed acid anhydride, and TP-5 of hexa hydroxy triphenylene and this invention, TP-29, TP-55, and the synthetic path of TP-85 are illustrated below in this example.

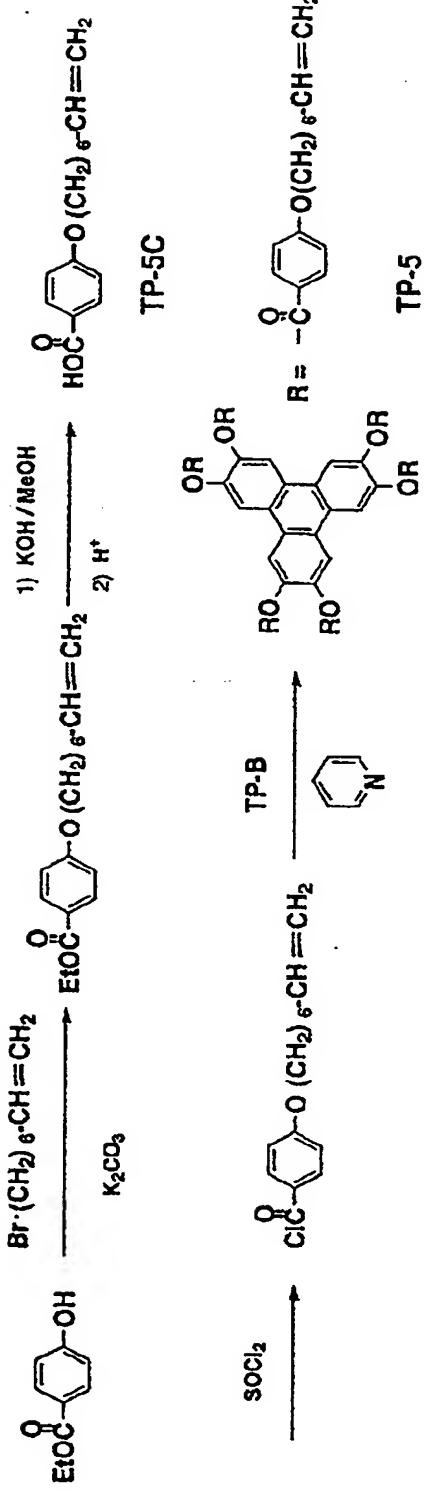
)113]

Formula 33]

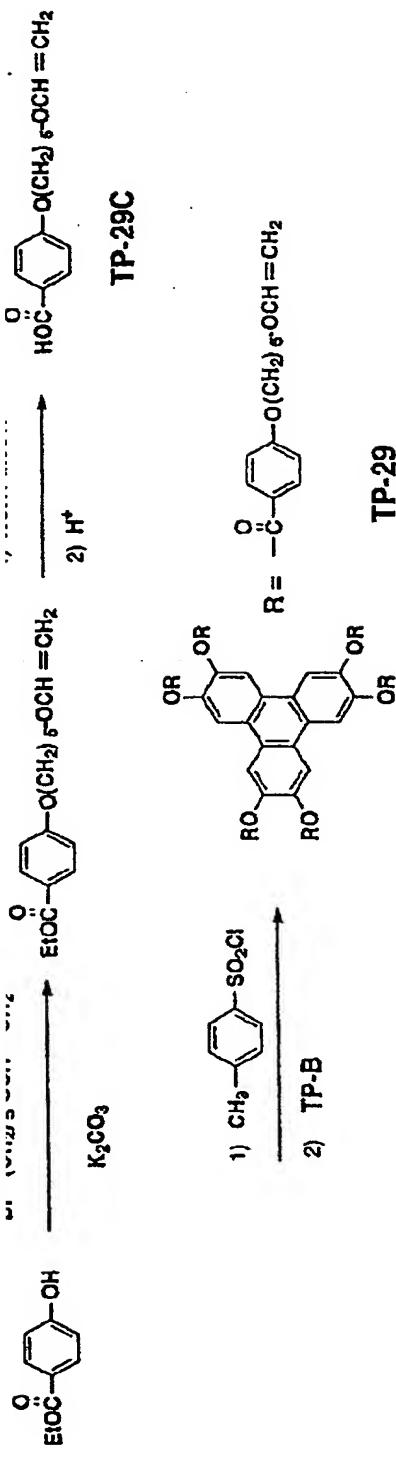


)114]

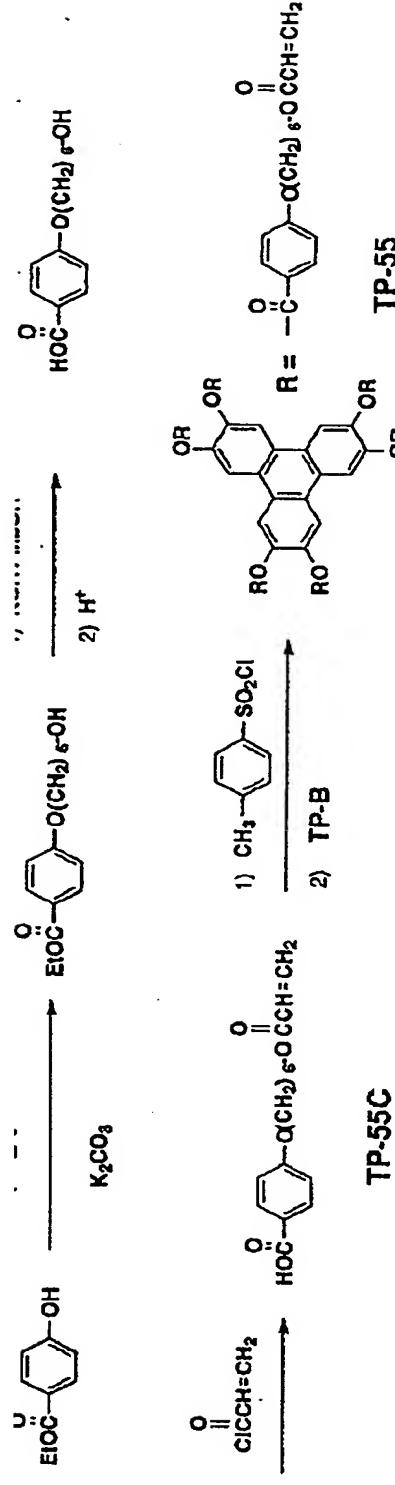
Formula 34]



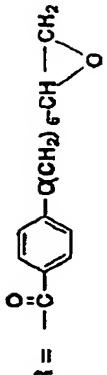
[115]  
[formula 35]



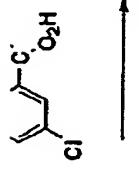
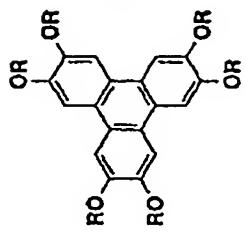
116]  
formula 36]



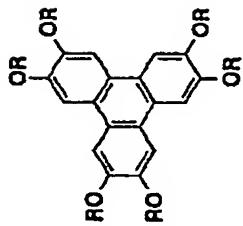
0117]  
Formula 37]



TP-85



TP-5



## [118] (Composition of a liquid crystal compound)

After stirring 455g and warm water 193mL violently by the mechanical stirrer by putting in to the composition 2, 3, 6, and 10 of TP-A, and the three-neck flask of 2L in which 11-hexamethoxy triphenylene (TP-A) carried out synthetic e-cooling and dissolving six monohydrates of ferric sulfate completely, 58.7g was added for 1 and 2-methoxybenzene. Next, concentrated-sulfuric-acid 882mL was gradually added under water cooling. It poured gradually 24 hours after and into iced water 9L, the reaction mixture was filtered with the glass filter 5 hours after, and 3.1g (83%) of rough crystals of TP-A was obtained.

P-A of the composition 2, 3, 6, 7, and 10 of TP-B and 48.1g of composition of 11-hexa hydroxy triphenylene (TP-B) as made to suspend in the dichloromethane of 850mL(s), and 150g of boron tribromide was added gradually. It poured 2 hours after and into iced water 7L, and cerite filtration was performed. After having taken out the specified substance containing cerite, making the methanol remelt and filtering, vacuum concentration of the filtrate was carried out. Filtration under reduced pressure of the obtained residue was carried out, the mixed solvent of an acetonitrile and chloromethane washed, and 32.7g (86%) of specified substance was obtained.

composition 4 of TP-5 -(7-OKUTE nil oxy)- 33.2g [ of para hydroxybenzoic acid ] and 8-BUROMO-1-octene 57.3g, 1.5g of potassium carbonate, and N,N-dimethylacetamide 200mL were put into the three necked flask of synthetic 20mL of a benzoic acid (TP-5C), and it stirred at 120 degrees C for 5 hours. Water 200mL was filled with the

action mixture after cooling, the ethyl acetate of 500mL extracted, and it washed twice by water 100mL. Sulfuric anhydride magnesium performed filtration after desiccation. The solvent was dissolved in methanol 100mL after vacuum concentration, methanol solution 20mL of 16.8g of potassium hydroxides was dropped gradually, and heating reflux was carried out for 2 hours. After cooling, filtration under reduced pressure of the produced crystal was carried out, and it was washed with water. 63.3g (85%) of TP-5C was obtained after desiccation.

.5g TP-5C and the thionyl chloride of 5mL(s) were put into the three necked flask of synthetic 100mL of 2, 3, 6, 7, 0, and 11-hexa (4-(7-OKUTE nil oxy-) benzoyloxy) triphenylene (TP-5), and heating reflux was carried out for 2 hours. The superfluous thionyl chloride was distilled off under reduced pressure after reaction termination. To this, the pyridine of 0.7g TP-B and 20mL(s) was added, and it stirred at the room temperature to it for 4 hours. It refined after distilling off a superfluous pyridine under reduced pressure using the silica gel chromatography, and TP-5 [ 2.73g (75%) ] were obtained.

Phase-transition-temperature measurement crystal phase-132 degree-C-Dr by identification data IR(cm-1):3080, 2940, 860, 1740, 1605, 1580, 1510, 14701420, 1315, 1250, 1170, 1120, 1070 and 1010, 900, 840, 760, 695DSC, and polarization microscope observation of TP-5 Liquid crystal phase-143 degree-C-Nd The -227 degrees-C-isotropy liquid of liquid crystal phases [0119] P-hydroxybenzoic-acid ethyl 33.2g, 5-BUROMO pentyl vinyl ether 58.0g, 41.5g of potassium carbonate, and N,N-dimethylacetamide 200mL were put into the three necked flask of synthetic 500mL of synthetic 4-(5-vinyloxy pentyloxy) benzoic acid (TP-29C) of TP-29, and it stirred at 120 degrees C for 5 hours. Water 200mL was filled with the reaction mixture after cooling, the ethyl acetate of 500mL extracted, and it washed twice by water 100mL. Sulfuric anhydride magnesium performed the desiccation back fault. The solvent was dissolved in methanol 100mL after vacuum concentration, methanol solution 20mL of 16.8g of potassium hydroxides was dropped gradually, and heating reflux was carried out for 2 hours. The produced crystal was carried out the \*\* exception after cooling, and the crystal was dissolved in water 1L. Filtration under reduced pressure of the crystal which added concentrated-hydrochloric-acid 25.7mL and deposited was carried out, and it was washed with water. 4.3g (TP-29C) (90%) of 4-(5-vinyloxy pentyloxy) benzoic acids was obtained after desiccation.

[120] 5.72g TP-29C, triethylamine 6.7mL, 1, and 2-dimethoxyethane 60mL were put into the three necked flask of synthetic 300mL of 2, 3, 6, 7, 10, and 11-hexa (4-(5-vinyloxy pentyloxy) benzoyloxy) triphenylene (TP-29), and at 0 degree C, methansulfonic acid chloride 2.75g was dropped slowly, and was stirred as it was for 2 hours. It returned to the room temperature, 4-dimethylaminopyridine 0.3g and TP-B 0.65g were added, and it stirred for 6 hours. The reaction mixture was filtered, filtrate was refined after vacuum concentration and using a silica gel column chromatography, and TP-29 [ 2.8g (82%) ] were obtained.

Identification data IR(cm-1):2960 of TP-29, 2955, 2880, 1765, 1690, 1625, 1605, 1520, 1495, 1480, 14351420, 1375, 360, 1290, 1260, 1220, 1195, 1140, 1110, 1080, 1050, 1030, 880, 810, 780, 740 [0121] P-hydroxybenzoic-acid ethyl 3.2g, 6-BUROMO hexanol 54.3g, 41.5g of potassium carbonate, N, and N-dimethylacetamide 200mL were put into the three necked flask of synthetic 500mL of synthetic 4-(6-acryloyloxy hexyloxy) benzoic acid (TP-55C) of TP-55, and it stirred at 120 degrees C for 5 hours. Water 200mL was filled with the reaction mixture after cooling, the ethyl acetate of 500mL extracted, and it washed twice by water 100mL. Sulfuric anhydride magnesium performed the desiccation back fault. The solvent was dissolved in methanol 100mL after vacuum concentration, methanol solution 20mL of 16.8g of potassium hydroxides was dropped gradually, and heating reflux was carried out for 2 hours. The produced crystal was carried out the \*\* exception after cooling, and the crystal was dissolved in water 1L. Filtration under reduced pressure of the crystal which added concentrated-hydrochloric-acid 25.7mL and deposited was carried out, and it was washed with water. 61.5g (86%) of 4-(6-hydroxy hexyloxy) benzoic acids was obtained after desiccation. 9.53g [ of 4-(6-hydroxy hexyloxy) benzoic acids ], N, and N-dimethylaniline 5.33g and dioxane 100mL were put into the three necked flask of 300mL(s), and at 60 degrees C, acrylic-acid chloride 3.98g was dropped slowly, and was stirred for 6 hours. It flowed into iced water 200mL after cooling, suction filtration of the depositing crystal was carried out, and 9.4g (80%) of TP-55C was obtained after washing and desiccation by the hexane.

[122] 5.67g TP-55C, triethylamine 6.7mL, 1, and 2-dimethoxyethane 60mL were put into the three necked flask of synthetic 300mL of 2, 3, 6, 7, 10, and 11-hexa (4-(6-acryloyloxy hexyloxy) benzoyloxy) triphenylene (TP-55), and at 0 degree C, methansulfonic acid chloride 2.75g was dropped slowly, and was stirred as it was for 2 hours. It returned to the room temperature, 4-dimethylamino pyridine 0.3g and TP-B 0.65g were added, and it stirred for 6 hours. The reaction mixture was filtered, filtrate was refined after vacuum concentration and using a silica gel column chromatography, and TP-55 [ 3.2g (80%) ] were obtained.

[123] Identification data IR(cm-1):2950 of TP-55, 2870, 1740, 1730, 1610, 1605, 1585, 1520, 1480, 14301415, 1375, 320, 1300, 1260, 1200, 1180, 1130, 1080, 1010, 990, 905, 850820 and 760, and -112 degrees-C-ND of 700 phase-transition-temperature measurement crystal phases by DSC and polarization microscope observation The -180 degrees-C-isotropy liquid of liquid crystal phases [0124] Synthetic TP-85 of TP-85 compounded TP-5 as a start raw material.

.67g TP-5 and 6.33g of m-chloro perbenzoic acids, and toluene 30mL were put into the three necked flask of synthetic 100mL of 2, 3, 6, 7, 10, and 11-hexa (4-(7, 8-epoxy octyloxy) benzoyloxy) triphenylene (TP-85), and it stirred at 60 degrees C for 2 hours. Depositing m-chloro perbenzoic acid was removed after cooling, it refined using the silica gel chromatography, and TP-85 [ 3.17g (82%) ] were obtained.

Phase-transition-temperature measurement crystal phase-114 degree-C-Nd by identification data IR(cm-1):3050,

940, 2850, 1740, 1605, 1580, 1510, 1470, 1420, 13201250, 1170, 1120, 1070 and 1010, 900, 840, 760, 695DSC, and polarization microscope observation of TP-85 The -220 degrees-C-isotropy liquid of liquid crystal phases [0125] Example 1 (verification of the orientation fixed effect by the light and the thermal polymerization of a liquid crystallinity compound)

Hereafter, the orientation fixed effect by the creating method, and its light and thermal polymerization of the optical anisotropy ingredient by the constituent containing the liquid crystal compound of this invention is explained. The slide glass for microscopes (the product S-7213 made from MATSUNAMI, size 76mmx26mm) was used as the substrate, liquid crystal compound DLC-27 were dissolved in the methyl ethyl ketone by 10wt(s)% concentration, the liquid was applied by 1000rpm by the spin coater, and the thin film of discotheque liquid crystal was made to form. This -- the product made from METORA -- FP-82 heat on a hot stage, and when you observe phase change behavior with a polarization microscope, pass a crystal phase-columnar phase -- it turned out that it became dark field at 147 degrees C, and transferred to the isotropic liquid phase. Next, liquid crystal compound DLC-27 were dissolved in the methyl ethyl ketone by 10wt(s)% concentration, and the 1wt% Michler's-ketone + benzophenone (weight ratio 1:1) was further added as a photopolymerization initiator. Since the columnar phase was stabilized at about 110 degrees C when the liquid was applied on the glass substrate by 1000rpm by the spin coater, it heated on the FP-82 hot stage made from METORA as similarly as the point and phase change behavior was observed with the polarization microscope, the black light (UVSL made from ULTRA-VIOLET PRODUCTS- 58 (16W)) was used, and optical exposure was carried out for 10 minutes. Change was not looked at by the gestalt of the columnar phase within the microscopic field in this condition. Then, when the temperature up was carried out further, at least 147 degrees C did not become dark field at all, and at least 200 degrees C were not transferred to an isotropic liquid phase after all.

[0126] That is, it is shown that polymerization immobilization of this fact was able to be carried out [ which DLC-27 of a disc-like compound call a columnar phase ], taking the high orientation condition of order nature very much, and turned out that it is a means very effective in the heat-resistant improvement in a thin film condition which maintained the orientation of a disc-like compound. 100-micrometer thickness film (FS[ by Sumitomo Bakelite Co., td. ]- 1300 and size 100mmx 100mm) of a polyether ape phon was used as the substrate, and the 0.1-micrometer elatin under coat was prepared, polyamic acid (SE made from Nissan Chemistry- 7210) was applied as orientation film on it, and it calcinated at 180 degrees C, and considered as the polyimide film. Rubbing of this polyimide film was carried out with the rubbing machine, and orientation ability was given. Liquid crystal constituent TP-38, TP-85, and TP-85+EGDGE (weight ratio 4:1) was respectively dissolved in the methyl ethyl ketone by 10wt(s)% concentration, the liquid was applied by 1000rpm by the spin coater, and the thin film of the discotheque liquid crystal of non-orientation was made to form. This was made into the film-like objects A, B, and C. After carrying out orientation of these and quenching them at predetermined temperature respectively, whenever [ each optical-axis tilt-angle / beta ], and deltan-d were measured by ellipsometry. The Shimazu work place ellipsometer (AEP-100) was made measurement at the transparent mode, the angular dependence of RETADESHON was searched for, and the direction of optimal 3 shaft-orientations refractive index and an optical axis was calculated by count from the value.

[0127] the shape of a film -- according to polarization microscope observation, object ATP-38 form a discotheque neumatic phase at about 130-183 degrees C. Then, the film-like object A is contacted on the metal roller heated in skin temperature of 190 degrees C for 10 seconds from a base material side, and the metal roller heated in skin temperature of 170 degrees C is made to contact for 30 seconds from a base material side immediately after that. Furthermore, the optical anisotropy ingredient of this invention was continuously obtained by making the metal roller adjusted to the skin temperature of 20 degrees C contact for 10 seconds. When polarization microscope observation of this sheet was carried out, having taken the discotheque pneumatic phase of a mono-domain was observed. Furthermore by measurement of ellipsometry, beta was deltan-d=125nm at 35 degrees whenever [ optical-axis tilt-angle ].

[0128] the shape of a film -- according to polarization microscope observation, object BTP-55 form a discotheque neumatic phase at about 143 degrees C. Then, the optical anisotropy ingredient of this invention was obtained by taking the metal roller which the film-like object A was contacted on the metal roller heated in skin temperature of 80 degrees C for 50 seconds from the base material side, and was adjusted to it immediately after that at the skin temperature of 20 degrees C contact for 10 seconds. When polarization microscope observation of this sheet was carried out, having taken the discotheque pneumatic phase of a mono-domain was observed. Furthermore by measurement of ellipsometry, beta was deltan-d=135nm at 32 degrees whenever [ optical-axis tilt-angle ].

[0129] the shape of a film -- according to polarization microscope observation, object CPT-85 form a discotheque neumatic phase at about 171-211 degrees C. Then, the optical anisotropy ingredient of this invention was obtained by taking the metal roller which the film-like object A was contacted on the metal roller heated in skin temperature of 80 degrees C for 50 seconds from the base material side, and was adjusted to it immediately after that at the skin temperature of 20 degrees C contact for 10 seconds. When polarization microscope observation of this sheet was carried out, having taken the discotheque pneumatic phase of a mono-domain was observed. Furthermore by measurement of ellipsometry, beta was deltan-d=155nm at 70 degrees whenever [ optical-axis tilt-angle ].

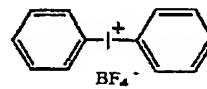
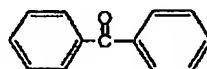
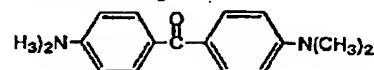
[0130] the shape of a film -- according to polarization microscope observation, the liquid crystal constituent of object TP-85 and EGDGE forms a discotheque pneumatic phase at about 109-158 degrees C. Then, the optical anisotropy ingredient of this invention was obtained by making the metal roller which the film-like object A was contacted on the

metal roller heated in skin temperature of 115 degrees C for 30 seconds from the base material side, and was adjusted so it immediately after that at the skin temperature of 20 degrees C contact for 10 seconds. When polarization microscope observation of this sheet was carried out, having taken the discotheque ~~isotropic~~ phase of a monodomain was observed. Furthermore by measurement of ellipsometry, beta was deltan-d=120nm at 44 degrees whenever [ optical-axis tilt-angle ].

0131] Next, a 1wt% Michler's-ketone + benzophenone (weight ratio 1:1) is added to each of liquid crystal constituent P-38, TP-55, TP-85, and TP-85+EGDGE (weight ratio 4:1) as a photopolymerization initiator. DONIUMU tetrafluoro borate is added. two liquid crystal constituents furthermore excluding TP-38 and TP-55 -- 1wt% diphenyl - Ito -- With, it dissolved in the methyl ethyl ketone respectively by 10wt(s)% concentration like the approach of the account of Gokami, the liquid was applied by 1000rpm by the spin coater, and the thin film of the discotheque liquid crystal of non-orientation was made to form. This was set to the film-like object AP, and BP, CP and DP. The structure of the three above-mentioned kinds of photopolymerization initiators is shown below.

0132]

Formula 38]



0133] These were respectively heated to the above-mentioned predetermined orientation temperature, the black light JVSL made from ULTRA-VIOLET PRODUCTS- 58 (16W) was used after 1 minute, and it cooled, after carrying out optical exposure for 2 minutes. Moreover, the above-mentioned film-like object C which carried out orientation as prepared by the same approach as one more sheet, heat-treatment was performed at 160 more degrees C for 4 hours, and this was made into the film-like object DPH. the above-mentioned film-like objects AP, BP, DP, and DPH - after measuring whenever [ each optical-axis tilt-angle / beta ], and deltan-d by ellipsometry, all the film-like objects A, B, C, AP, BP, DP, and DPH were left at 85 degrees C for 1000 hours, and whenever [ each optical-axis tilt-angle / beta ], and deltan-d were again measured by ellipsometry. The solubility to the methyl ethyl ketone of the film-like object before whenever [ before and behind compulsive heating of all film-like objects / optical-axis tilt-angle / beta ], deltan-d, and compulsive heating is shown in the following table 1.

0134]

Table 1]

表1

フィルム状物	強制加熱前		強制加熱後
	溶解性	光学特性 ( $\beta^\circ$ , $\Delta n \cdot d$ nm)	
A	○	35, 125	面状が悪化
B	○	32, 135	面状が悪化
C	○	70, 155	面状が悪化
D	○	44, 120	結晶が折出
AP	×	34, 122	35, 120
BP	×	32, 136	33, 133
CP	×	69, 148	69, 149
DP	×	41, 125	43, 125
DPH	×	43, 121	43, 121

0135] Although phase transition of the film-like object A was carried out to the isotropic liquid above 183 degrees C, the optical anisotropy was maintained and it stopped showing liquid crystallinity, i.e., the phase transition by heat, when if it heats the film-like object AP which is the photopolymerization film 10 minutes or more at 250 degrees C. Moreover, the film-like object which carried out the polymerization to that the liquid crystal constituent monomer of the invention can carry out the polymerization of the ability to point out for whether being \*\* from an upper table in the first place, maintaining the orientation in the light and the thermal polymerization process in the temperature after

rientation and the second is that thermal endurance is improving remarkably.

Example 3 (performance evaluation as phase contrast film aiming at angle-of-visibility expansion of a TN liquid crystal display device)

27-micrometer thickness film (the Fujifilm, size 100mmx100mm) of TAC was used as the substrate, the 0.1-micrometer gelatin under coat was prepared, denaturation poval was applied as orientation film on it, rubbing of this film was carried out with the rubbing machine, and orientation ability was given. The liquid crystal constituent which constitutes the film-like object CP indicated to Table 1 of an example 1 was used as the 10wt% methyl-ethyl-ketone solution, this was applied by 1000rpm by the spin coater, and the non-orientation layer of discotheque liquid crystal was made to form. then, the film-like object be contacted on the metal roller heated, the same approach of 115 degrees C, i.e., skin temperature, as the film-like object C, for 30 seconds from the base material side, after use the black light UVSL made from ULTRA-VIOLET PRODUCTS- 58 (16W)) and carry out optical exposure for 2 minutes in the condition, it cooled and the optical anisotropy ingredient of this invention be obtained. Polarization microscope observation of this sheet was carried out, and it checked having taken, the uniaxial orientation, i.e., the discotheque nematic phase, of a mono-domain. next, the angular dependence of contrast [ in / to a liquid crystal cell / the abnormality light of liquid crystal, the difference of the rate of usual state optical refraction, and the product of the gap size of a liquid crystal cell equip with the above-mentioned film-like object the TN liquid crystal cel whose angle of torsion is 90 degrees by 480nm, and / 30Hz square wave of 0-5V ] -- the product made from the Otsuka electron -- it measured by LCD-5000. The location of contrast 10 was defined as the angle of visibility, and it asked for the vertical and horizontal angle of visibility. Moreover, the contrast ratio when seeing from a transverse plane was measured. Here, the measured value of only the TN liquid crystal which does not equip with the above-mentioned film at all was written together. A result is shown in the following table 2. In addition, in drawing 4 , the arrow head expresses the direction of rubbing in the phase contrast film, and the direction of rubbing in a liquid crystal cell.

[136]

Table 2]

表2

位相差膜	視角特性	
	上-下	右-左
有り	7 5 ~ 7 9°	8 2 ~ 8 5°
無し	2 3 ~ 2 7°	3 3 ~ 3 6°

[137] In LCD which prepared the optical compensation sheet of this invention, the remarkable improvement of an angle-of-visibility property is attained like [ it is \*\*\*\*\* and ] from the upper table.

[138]

[Effect of the Invention] It is in \*\* that the optical anisotropy sheet with which the thin film obtained by the approach of this invention was excellent in thermal endurance with the sheet, and mono-domain nature was superior to the above example is offered, and the phase contrast film for liquid crystal display components in which a remarkable angle-of-visibility improvement is possible can be offered.

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\*\*\*\* shows the word which can not be translated.

In the drawings, any words are not translated.

## CLAIMS

## 7) [Claim(s)]

Claim 1] The manufacture approach of the thin film which consists of considering as the thin film which heats the is applied thin film and has the molecular orientation of optical anisotropy, carrying out a polymerization by subsequently adding light or heat energy, and forming the thin film of optical anisotropy after applying the coating liquid containing at least one sort of disc-like compounds which have the substituent which can carry out a polymerization by adding light or heat energy on this orientation film of the base material which has the orientation film on a front face and drying.

Claim 2] The manufacture approach of a thin film according to claim 1 that the molecular orientation of this optical anisotropy is a discotheque pneumatic liquid crystal layer.

Claim 3] The manufacture approach of a thin film according to claim 1 that this disc-like compound is a compound which is expressed with the following general formula (1) and has the reactant functional group P at the end of the dial side chain.

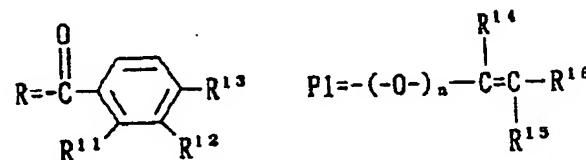
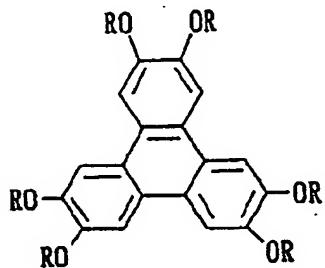
## general formula (1)

formula 1] Among a Rn-k-D-(L-P) k type, there is D at the core of a molecule and it expresses the radical of n organic functions which allot a total of n substituents R and substituent - (L-P) to a radial. Respectively k P independently An isocyanate radical, a thio cyanate radical, the amino group, An alkylamino radical, an arylamino radical, a sulphydryl group, a formyl group, An acyl group, a hydroxyl group, a carboxyl group, a sulfonic group, a phosphoryl group, a halo carbonyl group, A halo sulfonyl group, a halo phosphoryl group, an acryloyl radical, a ethacryloyl radical, A crotonyl radical, a vinyloxy radical, an epoxy group, an acetylenic group, a propargyl group, an arenyl radical is expressed. (n-k) R of an individual expresses the functional group which does not contribute to formation of a polymerization constituent independently respectively, L expresses respectively the radical or chemical bond which connects P and D independently, and n expresses the integer of 3-8, and k expresses the integer of 1-n.

Claim 4] The manufacture approach of a thin film according to claim 1 that this disc-like compound is expressed with general formula (2), a following general formula (3), or a following general formula (4).

## general formula (2)

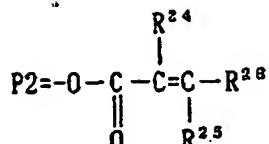
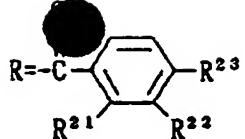
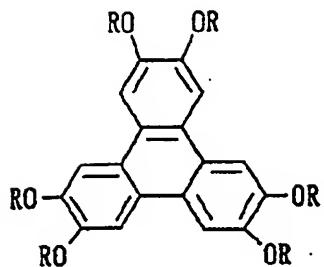
## formula 2]



though six benzoyloxy radicals combined with a triphenylene ring among a formula may differ even if they are usually the same -- the inside of it -- a piece at least has a substituent P1. R11 and R12 express a hydrogen atom or a ethyl group independently respectively, six R13 expresses an alkoxy group independently respectively, a piece at ast expresses the alkoxy group containing the above-mentioned substituent P1 of them, and R14, R15, and R16 of a substituent P1 express a hydrogen atom or an alkyl group independently respectively, and n expresses 0 or 1.

## general formula (3)

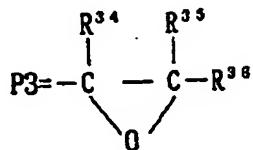
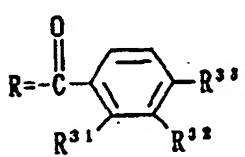
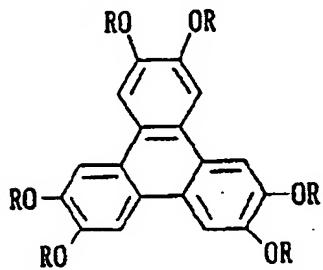
## formula 3]



though six benzoyloxy radicals combined with a triphenylene ring among a formula may differ even if they are mutually the same -- the inside of it -- a piece at least has a substituent P2. R21 and R22 express a hydrogen atom or a ethyl group independently respectively, six R23 expresses an alkoxy group independently respectively, and a piece at least expresses the alkoxy group containing the above-mentioned substituent P2 of them, and R24, R25, and R26 of substituent P2 express a hydrogen atom or an alkyl group independently respectively.

general formula (4)

[formula 4]



though six benzoyloxy radicals combined with a triphenylene ring among a formula may differ even if they are mutually the same -- the inside of it -- a piece at least has a substituent P3. R31 and R32 express a hydrogen atom or a ethyl group independently respectively, six R33 expresses an alkoxy group independently respectively, and a piece at least expresses the alkoxy group containing the above-mentioned substituent P3 of them, and R34, R35, and R36 of substituent P3 express a hydrogen atom or an alkyl group independently respectively.

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